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NOVEL CARBOXYLATES: AMINOOXYACETIC ACID DERIVATIVES

M.P. GEORGIADIS*

(Received June 9, 1975)

Summary

The preparation and properties of the title compounds syntehsized for biological screening, is presented. There is a marked similarity between the reported compounds and known anti-inflammatory drugs. Preliminary testing indicated that these compounds possess no significant anti-inflammatory activity. However, they were active as lens aldose reductase (LAR-LENS) inhibitors.

Theoretical Part

Advances of research in non-steroidal anti-inflammatory agents (NAA) as well as in the etiology and pathogenesis of rheumatoid arthritis have often been covered in the Annual Reports of Medicinal Chemistry.[1-4] Among the most important NAA compounds used are salicylates (aspirin), indomethacin, and arylalkanoic acids.[5] As starting materials for synthesis of the reported compounds Ia, Ib, Ic, II, III, carbonyl compounds were used having a carbon skeleton resembling the basic structure of those NAA mentioned above which are well-known drugs. The introduction of the carboxylate function was achieved by reacting the starting material with aminooxyacetic acid.

Chemistry: Aminooxyacetic acid being a derivative of hydroxylamine condenses with carbonyl compounds.[6-14] This condensation takes place very easily by stirring a reactive aldehyde, i.e. salicyl aldehyde, in 90% ethanol with one equivalent of aminooxyacetic acid hemihydrochloride in the presence of a basic reagent. Condensation with ketones requires refluxing. In the case of unreactive ketones benzene is used as solvent together with a Dean-Stark water trap to remove the water produced.

Biology: In a preliminary test it was found that compound III showed some anti-inflammatory activity, but in general the prepared compounds possessed no significant anti-inflammatory activity. However, they were found to be active in another respect. Almost every compound showed activity as an inhibitor of lens aldose reductase (LAR-LENS). 2-(o-Hydroxybenzylidene iminoxy) acetic acid (II), for example showed 57% inhibition of bovine LAR-LENS at 10^{-4} concentration. When the complete results of the screening tests are available more detailed information can be reported.

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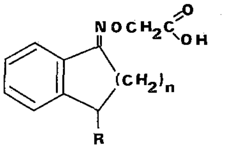

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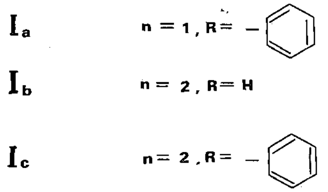

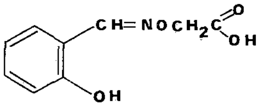

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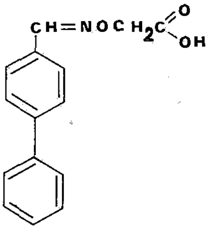


III

Experimental Part

Melting points were determined on a Thomas-Hoover apparatus. NMR spectra were obtained with a Varian A-60-A NMR spectrometer and are reported δ (ppm) calibrated against TMS. Al U.V. spectra were obtained on a Perkin-Elmer 350 spectrophotometer in ethanol solution. I.R. spectra were recorded on a Perkin-Elmer model 225 spectrophotometer.

Starting Materials: 4-Phenyl-tetralone and 3-phenyl-indanone were synthesized while other materials were purchased from Aldrich Chemical Co., Milwaukee, Wisconsin, U.S.A.

4,4-diphenyl-butyric acid: To freshly distilled ammonia (1200ml) freshly cut sodium 13.8g (0.6mol) was slowly added in small pieces and after the blue color was formed a small amount of ferric nitrate was added. Color change to grey is an indication of the sodium amide formation. To the gray sodium amide solution, diphenylmethane 100.8g (0.6mol) dissolved in absolute ether was added dropwise. Then 455g (0.3mol) of 3-bromopropionic acid dissolved in absolute ether was added dropwise. At the end of the addition of the acid the orange color of the sodium diphenylmethane disappeared. Then ammonia was allowed to evaporate on a steam bath and the ethereal mixture refluxed for ten minutes (ether may be added if required) and filtered to separate a solid which was dissolved in water. The water phase separated, washed with ether (2 to 3 times) and acidified with hydrochlorid acid, filtered and washed with water on the filter. The white solid obtained by the filtration crystallised from aqueous ethanol yielding 59g (81%) of 4,4-diphenyl butyric acid m.p. 103°-104° C.

3,3 diphenylpropionic acid: was prepared by the same method as 4,4-diphenyl butyric acid.

3-Phenyl-1-indanone: 3,3-Diphenylpropionic acid (2.5g) was heated with polyphosphoric acid at 125-130° C about one hour. The mixture was then poured into cold water and extracted with ether. The ether phase was neutralized with ammonium hydroxide, washed with water and dried over sodium sulfate. The solvent was then evaporated yielding 18g. (78%) of product as an oil. This oily product was kept for a while under reduced pressure, and crystallized by the addition of small amount of ethanol, yielding 12g. of 3-phenyl-1-indanone: m.p. 77-78°C, T.L.C. (CHCl$_3$) one spot,

I.R.: $\bar{\nu}_{max}^{CHCl_3}$ 1705 cm.$^{-1}$ U.V.: λ_{max}^{EtOH} 293(ε=2,640). 243 (ε=12050) mμ
N.M.R. data see table IIIa.

4-Phenyl-tetralone: was prepared by the same method as 3-phenyl-indanone.

2-(3-phenyl-1-indaniminoxy) acetic acid (Ia): A solution of 3-phenyl-1-indanone (about 10.4g.), aminooxyacetic acid hemihydrochloride (5.45g.) and sodium acetate (25g.) in 300 ml. of 90% ethanol were refluxed for 2 hours. The solvent was then evaporated under reduced pressure. The residue was slurried in an equal volume of water and made alkaline with 10% agueous sodium hydroxide solution. The unchanged phenylindanone was removed with ether extraction. The aqueous phase was made acidic to congo red indicator paper and the product was extracted with ether. Evaporation of ether yielded crude product (8.8g) which on recrystallization (ethanol-water) gave the title compound, analytically pure (6.6g.) m.p. 145.5°-146.5°,

I.R: $\bar{\nu}_{max}^{Nujol}$ 2900 (broad), 1733, inflexion at 1705, 1638, 1598, 1580, 1492, 762, 752, 702 cm^{-1}

U.V.: λ_{max}^{EtOH} 299 (ε = 5,580), 288 (ε = 5,500), 280 (ε = 4170), 256 (13,500)mμ.
N.M.R. see Table III.

2-(1,2,3,4-Tetrahydronaphthalen-1-aminooxy) acetic acid (Ib): To a solution of a-tetralone (7.3g. or 0.05 mol) and aminooxyacetic acid hemihydrochloride (5.4g. or 0.05 mol) in 300 ml of benzene, one equivalent of triethylamine (5.1g.) was added and the solution was refluxed for two hours using a Dean-Stark water trap to remove the water produced. Then the solvent was removed under reduced pressure. The residue was washed with water and crystallized from ether hexane to give about 4 g. of material which, on recrystallization, gave the title compound, analytically pure.

I.R. $\bar{\nu}_{max}^{CHCl_3}$ 2900 (broad), 1729 (s) 1763 (m), 1612 (w), 1588 (w),

I.R: $\bar{\nu}_{max}^{Nujol}$ 2900 (broad), 1730 (s), 698 (s), 1615 (w), 1585 (w), 1560 (w).

U.V.: λ_{max}^{EtOH} 258, (ε = 3175), 298 (ε = 2280) mμ.
N.M.R. data see table III.

2-(1,2,3,4-Tetrahydro-4-phenylnaphthalen-1-iminoxy) acetic acid (Ic): A mixture of 3 gms. of 4-phenyltetralone and 1.5 gms (one equivalent) aminoxyacetic acid hemihydrochloride and 5.5 gms of sodium acetate (3.3 equivalents) was refluxed in 150 ccs. of 90% ethanol for 2-½hours, then the solvent was evaporated *in vacuo.*

TABLE I. *Novel Carboxylates: Aminooxyacetic Acid Derivatives*

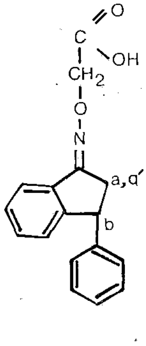
No.	Emp. Formula	M.P.	Calculated C	H	Analyses N	C	Found H	N	Yield
Ia	$C_{17}H_{15}NO_3$	145.5-146.5	72.58	5.37	4.98	72.88	5.29	4.57	64
Ib	$C_{12}H_{13}NO_3$	105-105.5	65.74	5.98	6.39	65.40	5.67	6.52	38
Ic	$C_{18}H_{17}NO_3$	146-147	73.20	5.80	4.74	73.50	5.67	4.80	66
II	$C_9H_9NO_4$	145-146	55.38	4.65	7.18	55.64	4.62	7.52	61
III	$C_{15}H_{13}NO_3$	165.5-166.5	70.58	5.13	5.49	70.42	5.32	5.42	72

TABLE II. *Carbonyl and Amino Infrared Absorption Bands.*[a]

Compound	C=O cm^{-1}	-C=N cm^{-1}
Ia	1733^{c}	1638^{c}
Ib	1728^{d}(s), 1763^{d}(w) 1730^{c}	1614^{d} 1616^{c}
Ic	1725^{d}(s), 1760^{d}(w)	1610^{d}
II	1738^{c}	1616^{c}
III	1734^{c}	1608^{c}

a I.R. were taken by 225-Perkin Elmer Instrument in nujol or chloroform. b) A. Richarson Jr. J. Med. Chem 7, 824 (1964) has reported that infrared absorption bands for aminooxyacetic acid derivatives are in the region 6.08-6.22 μ., The figure 6.2 μ or 1610 cm^{-1} being most frequent.
c Spectra obtained in nujol.
d Spectra obtained in chloroform.

TABLE III. *Aminooxyacetic Acid Derivatives - N.M.R. Spectra*

Compound	Number of ptotons	Type of protons	Chemical Shift δ (ppm)	Splitting pattern (J values in H_z)
 Ia (Solvent DMSO)	2	H-a	2.83	2 doublets
	2	H-a’	3.55	2 doublets
	1	H-b	4.60	2 doublets J a,a′ = 19 J a,b = 4.5 J a,b = 8.5
	2	$OCH_2C(=O)O$	4.70	singlet
	9	Aromatic	7.25	multiplet
	1	$C(=O)OH$	12.66	very broad

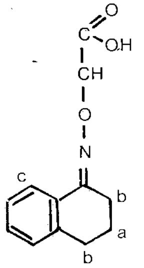
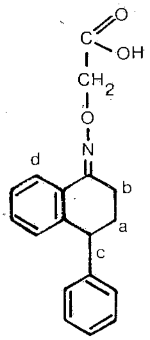
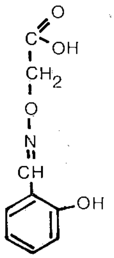
Compound	Number of protons	Type of protons	Chemical Shift δ (ppm)	Splitting pattern (J values in H_z)
 Ib (Solvent $CDCl_3$)	2	H-a	1.76	quintuplet } J - 6
	2	H-b	2.75	triplet
	2	$\mathrm{OCH_2C}{\begin{smallmatrix} =O \\ -O \end{smallmatrix}}$	4.66	singlet
	3	Aromatic	7.25	multiplet
	1	Aromatic	7.83	multiplet
	1	$-\mathrm{C}{\begin{smallmatrix} =O \\ -OH \end{smallmatrix}}$	broad	
 Ic (Solvent $CDCl_3$)	2	H-a	2.13	multiplet
	2	H-b	2.85	triplet (Jab = 6.5)
	1	H-c	4.13	triplet Jac = 6)
	8	Aromatic	7.25	multiplet
	1	H-d	8.08	multiplet
	1	$-\mathrm{C}{\begin{smallmatrix} =O \\ -OH \end{smallmatrix}}$	10.50	singlet
 II (Solvent DMSO)	2	$\mathrm{O-CH_2C}{\begin{smallmatrix} =O \\ - \end{smallmatrix}}$	4.73	singlet
	4	Aromatic	6.58-7.50	multiplet
	1	$\overset{H}{-C=}$	8.46	singlet
	2	$-OH + \mathrm{C}{\begin{smallmatrix} =O \\ -OH \end{smallmatrix}}$	9.66	broad

TABLE III. (continued)

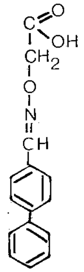
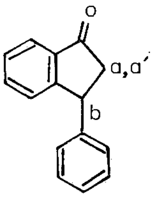
 III (Solvent DMSO)	2		4.73	singlet
	9	Aromatic	7.33-7.83	multiplet
	1	H —C=	8.40	singlet
	1	carboxylic	9.50	

TABLE IIIa *3-Phenyl-1-Indanone-N.M.R. Spectrum*

Compound	Number of protons	Type of protons	Chemical shift δ (ppm)	Splitting Pattern (J values in H_z)
	1	H-a	2.61	2 doublets
	1	H-a′	3.21	2 doublets
	1	H-b	4.55	2 doublets
				J aa′ = 19
				J ab = 4.5
				J a′b = 8
	8	H-aromatic	7.23	multiplet
	1	H-aromatic	7.80	multiplet

The residue was slurried in an equal volume of water and made alkaline with 10% aqueous sodium hydroxide solution. The unchanged ketone was removed by extraction with ether. The aqueous phase was acidified to congo red indicator paper by hydrochloric acid and the product was extracted with ether. The ether layer was washed until neutrality, dried and evaporated to dryness to yield 2.5g. of the title product as an oil which crystallized on standing m.p.146-147°C

I.R.: $\bar{\nu}^{CHCl_3}_{max}$ 3000 (broad), 1725 (s), 1760 (m), 1610 (w), 1595 (s), 1095 (s), 700 (s).

U.V.: λ^{EtOH}_{max} 260 (ε = 1330), 287 (ε = 2890), 297 (ε = 1550). mμ

N.M.R. see table III.

2-(o-Hydroxybenzylideniminoxy) acetic acid. (II) A mixture of salicyl aldehyde (2.4 g.), aminooxyacetic acid hemihydrochloride (2.1 g.) and sodium acetate (1.6g.) were dissolved in 60 ml. of ethanol and about 20 ml. of water and allowed to stand for several hours (overnight) and was evaporated to dryness under reduced pressure giving a white solid residue. This product was crystallized from water containing a small amount of ethanol yielding white crystals of salicylaldehyde o-carboxymethyloxime which is named according to C.A. as in the title; m.p. 145-146°C (2.4g.). The solvent used for T.L.C. was ethanolic ammonia -chloroform (1:1) . Ethanolic ammonia was made from 86 parts of ethanol, four parts of concentrated ammonium hydroxide, 10 parts of water.

I.R.: $\bar{\nu}_{\text{max}}^{\text{Nujol}}$ 2900 (broad). 1707 (m). 1617 (s), 1608 (s). 1556 (m), 1258 (s), 1098 (s).

U.V.: $\lambda_{\text{max}}^{\text{EtOH}}$ 262 ($\varepsilon = 2350$), 310 ($\varepsilon = 5070$). mμ

2-(p-Phenylbenzylideneaminoxy) acetic acid. (III) p-Phenylbenzaldehyde 5 g., aminoxy acetic acid hemihydrochloride 2.7 g. and 12.5 g. sodium acetate in 250 ml. ethanol (90%) yielded according to previously described procedure (see Ia) 3 g. of the title product, m.p. 165.5-166.5° C. (ethanol).

I.R.: $\bar{\nu}_{\text{max}}^{\text{Nujol}}$ 2900 (broad), 1734 (s), 1710 (m), 1605 (w), 1580 (w), 1558 (w), 1254 (w), 1102 (s).

U.V.: $\lambda_{\text{max}}^{\text{EtOH}}$ 287 ($\varepsilon = 32600$). mμ

N.M.R. see table III.

Περίληψις

Νέαι καρβοξυλικαὶ ἑνώσεις: Παράγωγα ἀμινοοξικοῦ ὀξέος

Ἡ ἐργασία αὐτὴ ἀφορᾶ τὴν σύνθεσιν νέων καρβοξυλικῶν ἑνώσεων καὶ συγκεκριμένως παραγώγων τοῦ ἀμινοοξικοῦ ὀξέος. Αἱ ἑνώσεις αὗται συνετέθησαν διὰ φαρμακολογικὴν ἐκτίμησιν. Κατὰ τὴν σύνθεσίν των ἐδόθη ἔμφασις ὥστε αὗται νὰ ὁμοιάζουν μὲ ἀντιφλογιστικὰ φάρμακα μεγάλης κυκλοφορίας, ὡς Indomethacin, Salicylates (Aspirin), Arylalkanoic acids. Προκαταρκτικαὶ δοκιμασίαι ἔδειξαν ὅτι αἱ ἑνώσεις αὐταὶ δὲν παρουσιάζουν ἀξιολόγους ἀντιφλογιστικὰς ἰδιότητας. Ἐν τούτοις παρουσίασαν διαφόρους βιοχημικὰς δράσεις. Οὕτω σχεδὸν ἅπασαι δροῦν ὡς χαλινωταὶ ἢ παρεμποδισταὶ τοῦ ἐνζύμου Lens aldose reductase (LAR-LENS) ἤτοι ρεδουκτάσης φακῶν (ὀφθαλμοῦ).

Ἐπὶ παραδείγματι, ἡ ἕνωσις 2(o-hydroxybenzyliden iminoxy) acetic acid, παρεμποδίζει τὴν δρᾶσιν τοῦ ὡς ἄνω ἐνζύμου κατὰ 57% εἰς παρασκευάσματα βοείου LAR-LENS εἰς συγκέντρωσιν 10^{-4} M.

References and Notes

1. Juby, P. and Hudyma, T.: *Ann. Rept. Med. Chem.* **7**, 208 (1972)
2. Rosenthale, M.: *Ann Rept. Med. Chem.* **3**, 214 (1973)
3 Rosenthale, M.: *Ann. Rept. Med. Chem.* **9**, 193 (1974)
4 Stewart Wong: *Ann. Rept. Med. Chem.* **10**, 172 (1975)
5 Dixon M. Woodbury and Fingl, E.: *"Analgetic-Antipyretics, Anti-inflammatory Agents and Drugs Employed in the Therapy of Gout"* in "The Pharmacological Basis of Therapeutics" Chapter 17 Fifth Edition, The Mac Millan Company, New York, 1975.
6 Wohl, A.: *Bull. Soc. Chem. France,* **2**, 2163 (1935)
7 Anchel, M. and Schoenheimer, R: *J. Biol. Chem.,* **114**, 539 (1936)
8 Borek, E. and Clarke, H.T.: *J. Am. Chem. Soc.* **58**, 2020 (1936)
9 Newman, M.S. Fones W. and Renoll, M.: *J. Am. Chem. Soc.* **69**, 718 (1947)
10 Holland, D.O.: *British Patent* **621**, 934 (1949): *Chem. Abstr.,* **44**, 6645 (1950)

11 Winternitz, F. and Lachazette, R.: *Bull. Soc. Chim. France*, 664 (1958)
12 Frank, A. and Riede, K.: *Monatsh.*, **92**, 725 (1961)
13 Dienes, L. Weinberger, H.J.: and Madoff, S.: *J. Bacteriol.*, **59**, 755 (1950)
14 Richardson, A.: *J. Med. Chem.* **7** 824 (1964)

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CONTRIBUTION TO THE STUDY OF GREEK BUTTER

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(Received July 5, 1975)

Summary

A modified new GLC method, permitting the rapid and complete determination of all the fatty acids of butter (C_4 to C_{18}) was devised. It was found that the fatty acid composition of milk fat is identical to that of butter and other products from the same milk sample. A systematic study of the fatty acid compositions of cow, ewe and goat butter samples indicated marked variations in the oleic, palmitic, lauric, myristic and capric acid contents of butters of different animal origin. A combination of these variations is expressed in the form of a relationship, usefull as a new constant for the identification of a butter sample's origin and its probable admixing or adulteration.

Introduction

Food chemistry has experienced many difficulties in differentiating between various kinds of milk from various sources and their products. Many investigators have faced this problem at various times, but most of proposed methods for the differentiation of milk or their products have proved "purely empirical", i.e. based solely on more or less dubious evidence and hence have not been widely accepted by analytical chemists; the procedures are time-consuming[1,2] and lead to untrustworthy results unless fresh samples are used.

Among the above methods are included those of R. Steineger and W. Austen[3] who observed varying solubilities of casein in ammonia for milk derived from goats or cows. Grosbusch and J. Krenn[4] treated milk derived from cows, goats and ewes with ammonium sulphate and ether and observed that casein rises to the upper layer, whereas the bottom layer is not always clear. But G. Panopoulos[5] following the above procedure obtained evidence for the presence of milk proteins in the bottom layer through a reaction with potassium ferrocyanide and concentrated acetic acid. Finally, Kohn observed that goat's milk when treated with concentrated sulphuric acid and n- amyl alcohol in a Gerber tube, is coaggulated to a large extent.

Other methods based on the analyses of the characteristics of butter include those of Fischer who reported that goat-milk butter possesses a low Reichert — Meissl number and a high Polenske number. R.K. Dons[6] observed a normal Reichert — Meissl and a high Polenske number for the butter from ewe — milk.

Attempts to differentiate butter from ewes, goats and cows were made by Galanos[7] and by Hilditch and Williams.[8]

Finally Bosworth and Van Slyke showed that goat-milk contains phosphates such as tricalcium, trimagnesium and monopotassium (but no monomagnesium or bipotassium) and potassium citrate (but no sodium citrate, sodium chloride or potasium or calcium), which are absent in cow milk.

To cope with the problem of the differentiation of milk and its products it was necessary to device a quick, accurate and modern procedure, independent of the freshness of the sample tested.

To this end we undertook an extensive and systematic study of Greek butter samples by gas chromatography. The fat content from a large number of standard butter samples derived from milk of known, unambiguous origin, was subjected to trans-esterification by a new rapid procedure (as described in the experimental part). The esters thus obtained were subjected to a "modified gas-chromatographic analysis" and at the same time attempts were made to choose the right conditions.

J.P. Wolff[9] considered the gas chromatographic analysis of the methyl — esters of butter, extremely difficult, due to the fact that the methyl — ester of volatile butyric acid cannot be satisfactorily analysed by G.L.C. The use of propyl-esters was thus suggested for this purpose.

After continued efforts we were successful at obtaining and separating butyric, linoleic and linolenic acids, after careful control and choice of proper chromatographic conditions (Fig. 1).

Additional G.L.C. analyses were carried out on milk, yogourt, cheese and butter cream prepared from the same milk samples. The results were similar to those obtained for butter. Suitable gas chromatograms were also obtained from fatty substances suitable for butter adulteration and from samples of adulterated butter. (Fig. 2).

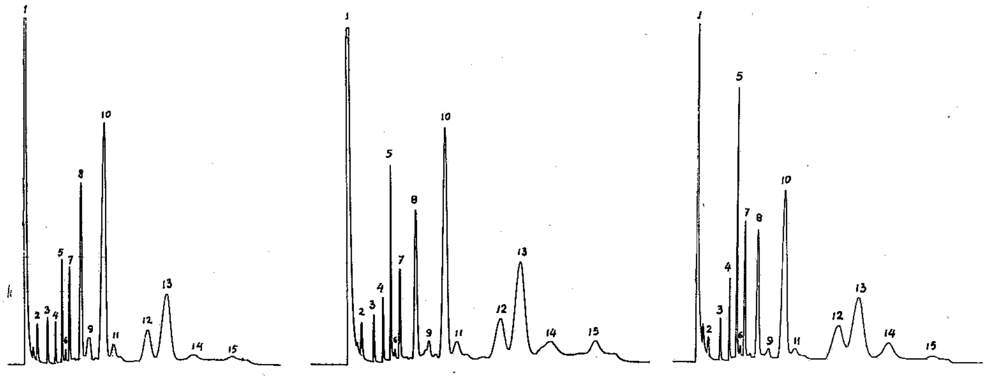

FIG. 1. Gas-liquid chromatograms of cow butter (A), ewe butter (B) and goat butter (C). Numerals indicate the fatty acid methyl exters in the order of increasing retention times, as follows:

1. Solvent front
2. butyric ester
3. caproic »
4. caprylic »
5. capric »
6. caprinoleic ester
7. lauric »
8. myristic »
9. myristoleic »
10. palmitic »
11. palmitoleic ester
12. stearic »
13. oleic »
14. linoleic »
15. linolenic »

For experimental conditions, see text.

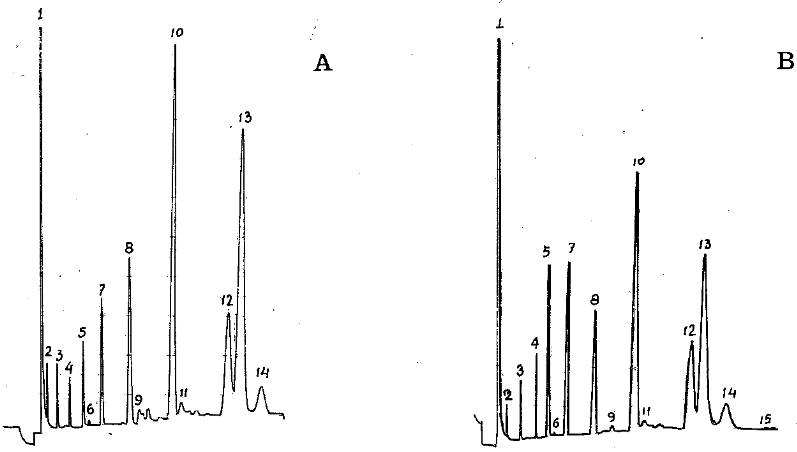

FIG. 2. *Gas-liquid chromatograms of adulterated butter samples:* A, 85% cow butter, 10% refined olive oil, 5% coconut seed oil. B, 85% ewe butter, 10% refined olive oil, 5% coconut seed oil. For notation and experimental conditions, see Fig. 1.

Materials and methods

All materials employed in this work, were AR or ANALAR grade reagents. All solvents were further purified by distillation where applicable. Reagents paraffin, glycerol, n-heptane were obtained from Merck-Germany and sodium hydroxide, sulphuric acid, methanol, perchloric acid, sodium sulphate anhydrous e.t.c. were obtained from Riedel de Häen A.G. - Germany.

For gas chromatography an Aerograph 1520 flame-ionisation G.C. was employed equipped with a Westronics L D 11 A recorder and a Planimeter Allbrit area intergator. An automatic Dinfotronics CRS 208 digital integrator was also employed for area measurements. The column used was a DEGS 15% (on chromosorb W, 60-80 mesh) 7 feet long and 1/8 inches external diameter.
Carrier gas: Nitrogen, 20 cc/min. Chart speed: 20 inches per hour. Output attenuation: 8. Column temperature: 110-215° C. Program (initial 110° C, after butyric acid raise to 190° C, after myristic acid raise to 205° C and finally following oleic acid raise to 215° C). Injector temperature: 245° C. Detector temperature: 285° C.

Time required for completion of analysis 45 mins (i.e. esterification, 15 mins and chromatogram, 30 mins).

Additional gas chromatograms were obtained with a TRACOR 550-flame ionization gas chromatograph with programming facilities, and equipped with a Westronics MT 21 S N 1390 recorder. The column used was a DEGS 15% (on chromosorb W 8‰) 6 feet long and ext, diam, 1/4 inches, (S.S. F.D. 5732). Carrier gas: Argon, 40cc / min. Chart speed: 20 inches per hour. Input attenuation: 10^3. Output attenuation: 16. Input, detecor and column temperatures were as stated above.

Experimental

A special mixer was used for the preparation of a large number of standard butter samples, derived from milk of cows, ewes and goats of known and unambiguous origin. The samples were melted on a water bath, the upper fatty layer was obtained and filtered through a flutted filter paper. The butter samples were analyzed for:

a) Butter - refractometer number at 40° C[11]
b) Reichert - Meissl number[7,10,11]
c) Polenske number[7,10,11]

Transesterification was carried out according to the following procedure:[11,12] 0,5 gr of melted butter sample are filtered as above in a 50 -ml ground glass conical or round bottomed flask. To this 10ml of a 0,5 N solution of sodium methoxide are added together with boiling chips and boiled under reflux on a waterbath for about 10 minutes. Subsequently 0,8 ml of perchloric acid (70%) are added, boiled for 2 minutes, 5ml of n-heptane are added and boiled for 2 further minutes.

The contents are then transferred to a 50 ml ground glass stoppered volumetric cylinder containing 10 ml of a saturated saline solution. It is shaken vigorously for 30 sec and the upper layer is pipetted into a ground glass stoppered test-tube containing anhydrous sodium sulphate. A quantity amounting to 1-1,5 μl is used to run all subsequent gas chromatograms.

Results and discussion

Classical analyses furnished the following results.

I. Cow butter.
Butter-refractometer number at 40° C :............. 40,0 - 42,8
Reichert - Meissl number :................................. 26,2 - 29,1
Polenske number :.. 1,6 - 4,6

The corresponding literature values[13] are 40,0 - 45,5 24,5 - 32,8 and 1,5 - 3,7 respectively.

Other values[8] include: Reichert - Meissl number, 33 - 36, Polenske number, 1,3 - 3,5.

II. Ewe Butter.
Butter - refractometer number at 40°C :............. 41,3 - 43,7
Reichert - Meissl number :................................. 24,4 - 32,5
Polenske number :.. 3,1 - 4,9

The corresponding literature values[8] for Reichert-Meissl and Polenske numbers are 22 - 33 and 2,2 - 6,9 respectively.

III. Goat butter.
Butter - refractometer number at 40°C :............. 40,7 - 42,2
Reichert - Meissl number :................................. 20,5 - 26,1
Polenske number :.. 4,7 - 6,0
Literature values[8] are
Reichert - Meissl number :................................. 20 - 29
Polenske number :.. 3,2 - 9,8

In the Greek Code of Regulations for Foodstuffs, Beverages e.t.c.[14] the following values are reported for butter in general:

Butter - refractometer number at 40°C :.................. 41 - 44
Reichert - Meissl number :............................ 26 and higher
Polenske number :.. 3 - 4

Comparing the above data with the results of this work, we arrive to the conclusion that some discrepancies do occur, which however are justifiable as it is explained in the litterature. For example, it is reported[15] that animals fed with coconut-oil cakes, furnish butter with a high Polenske number and a low Reichert - Meissl number. For this purpose a value of 24 has been agreed as a minimum for the Reichert - Meissl number for butter. Poorly fed animals[15] or during lactation may furnish butter with a Reichert-Meissl number as low as 22 and rarely 20 or less.

The fatty acid content of butter is enriched with unsaturated fatty acids when animals are fed with seed oil cakes. Thus e.g. dilauromyristin, which is contained in coconut-seed oil up to 15%, can finally be present in the butter derived from animals fed on such seed-oil cakes.

Feed rich in linoleic acid[9] can provide butter with higher linoleic acid content and similarly, cop rah rich feed practically doubles the lauric acid content of butter.

Animals fed on cotton-seed oil cakes[7] which possess a high iodine value, furnish butter with a low Reichert-Meissl number. Animals fed on clover, beetroots etc. on the other hand, furnish butter with high Reichert-Meissl and Polenske numbers, due to the fact that such feeds tend to increase the content of volatile fatty acids.

The percentage content of volatile fatty acids in butter can fluctuate during lactation. Thus collostrum contains a small percentage of volatile fatty acids, which

TABLE I.
Present data for fatty acid percentage composition of butter compared to literature data.[8,9,10]

Fatty Acids	Cow		Ewe		Goat	
	Present values	Literature values	Present values	Liter. values	Present values	Literature values
$C_{4:0}$ Butyric	1,0- 2,5	3,0- 3,7	0,7- 2,1	2,8	0,9- 1,4	3,0
$C_{6:0}$ Caproic	1,2- 2,6	1,4- 2,0	1,0- 2,6	2,6	1,4- 2,5	2,5
$C_{8:0}$ Caprylic	1,0- 2,1	0,5- 1,5	1,0- 3,1	2,2	2,3- 3,4	2,8
$C_{10:0}$ Capric	2,5- 4,7	1,9- 2,6	7,2- 9,6	4,8	12,3-13,7	10,0
$C_{10:1}$ Caprinoleic	0,1- 0,3	0,1- 0,3	0,1	0,1	0,1- 0,3	0,3
$C_{12:0}$ Lauric	2,0- 4,3	1,7- 3,7	3,0- 4,2	3,9	3,4- 7,4	6,0
$C_{14:0}$ Myristic	7,5-14,1	7,9-12,1	9,5-14,2	9,7	8,0-11,3	12,3
$C_{14:1}$ Myristoleic	1,1- 3,2	0,6- 1,6	0,5- 2,0	0,6	0,7- 1,2	0,8
$C_{16:0}$ Palmitic	29,1-40,8	25,3-29,0	25,6-34,7	23,9	26,7-32,7	27,9
$C_{16:1}$ Palmitoleic	1,2- 2,6	2,4- 5,0	1,0- 2,3	2,2	0,9- 1,4	2,6
$C_{18:0}$ Stearic	6,2-17,0	9,2-12,7	8,0-13,4	12,6	8,5-16,1	6,0
$C_{18:1}$ Oleic	20,5-28,8	26,7-34,0	17,2-26,4	26,3	17,1-20,6	21,1
$C_{18:2}$ Linoleic	1,3- 5,1	3,6- 4,0	2,2- 7,2	5,2	2,3- 5,7	3,6
$C_{18:3}$ Linolenic	0,3- 1,5	0,3- 1,7	0,2- 3,3	1,9	0,2- 0,8	0,2

increases during the first months of lactation and subsequently, the water soluble higher volatile fatty acids are gradually reduced.

A considerable reduction in the volatile fatty acid content is observed towards the end of lactation. Thus ewe and goat butter contain a higher percentage of insoluble volatile fatty acids (and a higher Polenske number) when compared to cow butter.

From the foregoing becomes evident that the volatile fatty acid percentage composition of butter, and consequently the corresponding Reichert - Meissl number (for water soluble volatile fatty acids) and Polenske number (for water insoluble volatile fatty acids) depends largely on the nature of animal feed and on all above mentioned factors.

The systematic study of the constitution of Greek butter has thus been rendered feasible for the first time, using the rapid gas chromatographic method for the quantitative determination of the fatty acids of butter (acids with 4 through 18 carbon atoms), developed in this work.

Our data demonstrated in general that the fatty acids contained in either milk or butter and / or any products, are uniquely identical. Thus for all products derived from the same sample of milk (i.e. butter, cream, cheese, yougourt e.t.c.) the percentage constitution of fatty acids was found identical to that of the fat extracted from the original milk sample.

A careful comparison and consideration of these data leads to some very interesting observations and conclusions, concerning the variations in the relative abundance of some of the constituent fatty acids in butter, depending on the kind of animal used as the source of milk. Namely, such variations in the oleic, palmitic, lauric, myristic and capric acid contents seem to satisfy a certain relationship (see below), useful for the identification of the origin of a butter sample. These data indicate that the decrease in oleic acid content is largely proportional to the decrease in palmitic and lauric acid contents with a simultaneous increase in the content of capric acid. Similarly, the increase of myristic acid content of ewe butter is followed by an even higher increase in the percentage of capric acid.

The above observations enable one to understand the mechanism by which living organisms synthesize fats of low melting point. Limitted ability to produce oleic acid is balanced by a reduction in the percentage of the higher saturated fatty acids (which possess high melting points), with a concomitant increase in the production of lower fatty acids, which although saturated, possess lower melting points.

On the basis of the foregoing data and conclusions a usefull new constant C, characteristic of the origin of butter, may be defined as follows:

$$C = \frac{100 \times [\text{capric acid}]}{[\text{Lauric} + \text{Palmitic} + \text{Oleic}]}$$

Values of C, according to our data vary as follows

Cow butter: 4,8 - 7,4; Ewe butter: 14,2 - 17,5; Goat butter: 22,3 - 25,7.

Therefore, it is obvious that this new constant satisfactorily identifies the origin of butter (or milk products) whithin well defined limits, and that mixed butter samples of any nature and origin would give a value of C lying in between the above well defined limits. In addition, butter adulteration (by means of coconut seed oil, cotton seed oil, monoglycerides e.t.c.) could safely be predicted, on the basis of the above new constant, combined with a comparison of the percentage composition of individual fatty acids. Most helpfull among the individual fatty acid contents for the identification of the origin of butter is the capric acid content, varying as follows: Cow butter: 2,5 - 4,7%; Ewe butter: 7,2 - 9,6%; Goat butter: 12,3 - 13,7%.

In addition, a high proportion of lauric acid (4,5 - 7,5%) strongly suggests, goat butter, whereas a high proportion of myristic acid (higher than 11,5%) suggests cow or ewe butter.

Περίληψις

Συμβολὴ εἰς τὴν μελέτην τῶν ἑλληνικῶν βουτύρων.

Διεμορφώθη νέα ταχεῖα ἀεριοχρωματογραφικὴ μέθοδος, διὰ τῆς ὁποίας ἐπετεύχθη ἀκριβὴς ποσοτικὴ ἀνάλυσις ὅλων τῶν λιπαρῶν ὀξέων τοῦ βουτύρου μεταξὺ 4 καὶ 18 ἀτόμων ἄνθρακος. Διὰ χρησιμοποιήσεως τῆς ὡς ἄνω ἀεριοχρωματογραφικῆς μεθόδου, κατεδείχθη ἡ ταυτότης τῆς συστάσεως τῶν λιπαρῶν ὀξέων τῶν διαφόρων προϊόντων γάλακτος τῶν προερχομένων ἐκ τοῦ αὐτοῦ δείγματος γάλακτος. Ἐμελετήθη συστηματικῶς ἡ σύστασις τῶν λιπαρῶν ὀξέων τῶν ἑλληνικῶν βουτύρων, ἐνδεικτικῶς δὲ καὶ τινων προϊόντων ἐκ γάλακτος ἢ νοθευμένων βουτύρων. Ἡ μελέτη τῶν ληφθέντων ἀναλυτικῶν ἀποτελεσμάτων ἀπεκάλυψεν ἐνδιαφερούσας διαφορὰς τῶν σχετικῶν ἀναλογιῶν ὡρισμένων ἐκ τῶν συστατικῶν τοῦ μείγματος τῶν λιπαρῶν ὀξέων τοῦ λίπους τοῦ βουτύρου, ἀναλόγως τοῦ ζώου προελεύσεώς του. Κατὰ τὸν τρόπον αὐτὸν προέκυψαν ἐνδιαφέρουσαι ἐνδείξεις περὶ τοῦ τρόπου μὲ τὸν ὁποῖον οἱ ζῶντες ὀργανισμοὶ ἐπιτυγχάνουν νὰ σχηματίζουν λίπος τοῦ ἀπαιτουμένου χαμηλοῦ σημείου τήξεως. Ἐπὶ τῇ βάσει τῶν γενομένων παρατηρήσεων προτείνεται νέα σταθερὰ διὰ τὸν καθορισμὸν τοῦ εἴδους τοῦ βουτύρου (ἢ γάλακτος καὶ προϊόντων τούτου), ἡ ὁποία ἔχει πολὺ σαφῆ καὶ στενὰ ὅρια διακυμάνσεως.

References and Notes

1 Birbili - Ninni M.: Doctoral dissertation, University of Athens, Athens, Greece (1950).
2 Ninnis L.N.: Doctoral dissertation, Univercity of Athens, Athens, Greece (1941).
3 Steineger R. und Austen W.: *Zeit Unters, Nahr. und Genussm.* 7, 396, (1904); **45**, 382, (1923).
4 Krenn J.: *Östereische Milchwirts,* **37**, 231, (1930).
5 Galanos S. D.: *Food Chemistry,* Vol. 3, p. 149 and 243, Athens (1948).
6 Dons R.K.: *Zeit. Unters. Nahr. und Genussm.,* **15**, 72, (1908).
7 Galanos S.D.: *Food Chemistry,* Vol. 2, p. 105 Athens (1948).
8 Hilditch T.P. and Williams P.N.: *The chemical constitution of natural fats,* (4th edition), p. 510 Chapman and Hall, London, (1964).
9 Wolff J.P.: *Manuel d'analyse des corps gras,* p. 392, Azoulay, Paris, (1968).
10 Galanos D.S. and Voudouris E.C.: *Introduction to food analysis,* p. 138 Athens, (1971).
11 *J.A.O.C.S., American Oil Chemist's Society,* Revised 1973, Method Ce-2-66,
12 *Gas chromatography abstracting service,* Preston Technical Abstracts Co, No card 66 — 1888/1-1-66.
13 Pearson D.: *The chemical analysis of foods,* (6th Edition), p. 472, J. and A. Churchill, London, (1970).
14 *Greek Code of Regulations for Foodstuffs, Beverages and Common Use Items,* p. 156 Athens, (1972).
15 Williams K.A.: *Oils, fats and fatty foods,* (3rd Edition), p. 196, J. and A. Churchill, London, (1966).
16 Pointurier H.: *Adda J., Beurrerie industrielle,* p. 20, La maison rustique, Paris, (1969).

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POLYCONDENSATION OF 2,5- FURANDICARBOXYLIC ACID CHLORIDE WITH AROMATIC DIAMINODICARBOXYLIC ACIDS

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Summary

Solution polymerisation and interfacial polymerisation techniques are carried out to prepare new poly(furylene)benzoxazinones by reaction of 2,5-furandicarboxylic acid chloride with aromatic diaminodicarboxylic acids. A new poly(furylene) benzoxazinone with fairly good thermal stability is prepared in two steps with 3,3'-dicarboxybenzidine. However all the procedures applied to prepare the corresponding polymers with 4,6-diamino-isophthalic acid or 2,5-diamino-terephthalic acid were less succesful and the probable reasons of the non extent polymerization are discussed. The methods of the preparation of the monomers with some modifications, as well as, the polymerization conditions applied with a study of some reaction variables are described and the results are discussed.

Key words: Poly(furylene)benzoxazinone, Poly(furylene)benz-bis(oxazinones), Polyamic acids, High-temperature polymers.

Introduction

In the past few years new polymers capable of prolonged use at elevated temperature have been prepared.[1,2] This field of polymers was greatly developed because of their use in specific requirements of space exploration, supersonic flight and elsewhere. The stable at high temperature polymers are mostly heterocyclic chains which can be obtained, among other procedures, by reaction of a tetrafuctional aromatic compound with a dicarboxylic acid or a derivative of it.

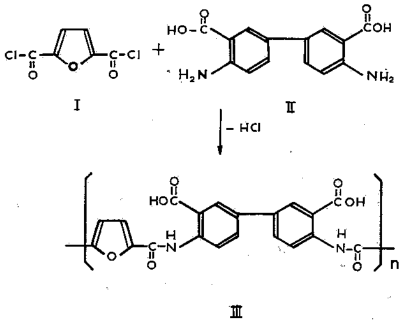
This paper deals with the use of 2,5-furandicarboxylic acid (chloride) to prepare new polymers stable at high temperature. The use of this acid which is obtained from 2-furoic acid, a by-product of Cannizzaro reaction of furfurol, was intentionally chosen according to an extensive project[3] to evaluate the furoic acid as a raw material.

High-temperature poly(furylene)benzimidazoles,[4,5] poly(furylene)benzoxazole[6] and poly(furylene)benzothiazole[7] have already been obtained by reaction of 2,5-furandicarboxylic acid (chloride or phenylester) with 3,3-diaminobenzidine,[4] 3, 4, 3', 4'-tetraamino-oxydiphenylene,[5] 3,3'-dihydroxybenzidine[6] and 3,3'-dimercaptobenzidine,[7] correspondingly.

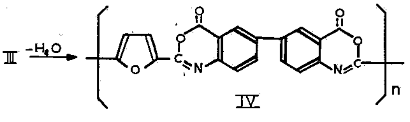
As no poly(furylene) benzoxazinones or poly(furylene) benz-bisoxazinones are reported in the literature this paper deals with the preparation of these polymers (IV, VII, VIII) by using as a tetrafuctional aromatic compound 3,3'-dicarboxybenzidine (II), 4,5-diamino-isophtalic acid and 2,5-diaminoterephthalic acid.

The procedures for the preparation of these aromatic diamino-dicarboxylic acids are described in the experimental section and several modifications applied, results and comments are reported there.

In order to obtain the mentioned new polymers low temperature solution polymerization as well interfacial polymerization techniques were followed. Thus by a similar process of low temperature solution polymerization as used with isophthaloyl chloride,[8] using 2,5-furandicarboxylic acid chloride (I) and 3,3′-dicarboxybenzidine (II), an open chain polyamic-acid (III) was obtained (eq. 1). In a second step this polymer underwent thermal cyclodehydration to yield poly(furylene)benzoxazinone (IV) (eq. 2).

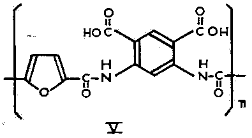


eq. 1

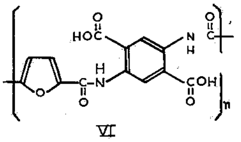


eq. 2

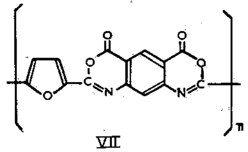
In analogous processes using 4,6-diamino-isophthalic acid or 2,5-diaminoterephtalic acid the corresponding polyamic-acids (V, VI) and poly(furylene) benz-bis-oxazinones (VII, VIII) should have been obtained.



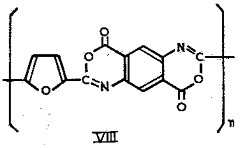
V



VI



VII



VIII

However, these polymers (V, VI, VII) have been produced only with a very low value of inherent viscosity even when more drastic reaction conditions and interfacial polymerizations with immiscible organic solvents were applied.

The polymerization procedures applied are described in the experimental section. The results of the study of some reaction variables with the results and conclusions of this paper are discussed.

Experimental

Instruments: All the melting points were taken on a Büchi melting point apparatus, are uncorrected and referred to °C. Elemental analyses were performed with a Perkin — Elmer 240 Elemental Analyzer apparatus. Infrared spectra were recorded with a Higher and Watts (Infrascan) spectrophotometer using potassium bromide disks or nujol mulls. All inherent viscosities were measured with an Ubbelohde viscometer and are referred to 0.5% concentration in conc. sulfuric acid at 25° C. Differential thermal analyses (DTA) and thermal gravimetric analyses (TGA) were obtained with a MOM (Budabest) derivatograph, using 200 mg of a sample in a nitrogen atmosphere and a heating rate 5° C/min.

Monomers.

2,5-Furandicarboxylic acid chloride (I). It was prepared analogously to terephthaloyl chloride[9] by refluxing 2,5-furandicarboxylic acid with thionyl chloride for 24hrs. White large needles. Yield 50%, mp 78-79° (Lit.[10] mp 79-80°).

2,5-Furandicarboxylic acid was obtained from 2-furoic acid via methyl-2-furoate[11] and methyl 5-(chloromethyl) -2-furoate[12] to 2,5-furandicarboxylic acid.[13]

3,3′-Dicarboxybenzidine (II). It was prepared by reduction[14] of o-nitrobenzene to 2,2′-hydrazobenzedicarboxylic acid and benzidine rearrengement[15] of the latter to crude II (Yield 80%, mp 292° dec.). Highly purified II was received from the recrystallized hydrochloric salt ($II \cdot 2H_2O \cdot 2HCl$, colourless needles) by treating with water and a solution of sodium acetate. Yellow lightly greenish powder, dried in vacuum. Yield 52%, mp 297° dec. (Lit[15] mp 300° dec.).

The infrared spectrum showed absorption bands at 3490, 3380 cm^{-1} (NH) and 1675 cm^{-1} (C=0) and the elemental analysis was in concordance with the formula.

Calcd for	$C_{14}H_{12}N_2O_4$	C, 61.76;	H, 4,44;	N, 10.29%
	Found	C, 61.81;	H, 4.35;	N, 10.39%

Notes. Benzidine rearrangement with dilute hydrochloric acid[14] gave nearly a theoretical yield but afforded an impure product. Preparation of pure II according to a patent[16] was unsuccessful in our experiments and the purification of II through its triethylamine salt[17] did not prove to be more effective than that through hydrochloric salt.

4,6-Diamino-isophthalic acid. It was prepared from 4-amino-m-xylene (Fluka, b_{11} 98°) by the following steps,[18] with some modifications to the original methods. a) 4-Amino-6-nitro-m-xylene. The nitration[19] was carried out at low temperature[20] to improve the yield. Large orange needles reclystallized from alcohol. Yield 54%, mp 121-123° (Lit[18] mp 123°). b) 4,6-Diamino-m-xylene. The reduction of the above compound (0.5 mol) was carried out with iron (85 g), instead of tin,[21] and hydrochloric acid (50 ml conc. and 750 ml water), analogous to the reduction of 4,6-dinitro-m-xylene.[22] After removal of iron by filtration and addition sodium carbonate the acidified filtrate containing the free diamine afforded by addition acetic anhydride (130 g): c) 4,6-Diacetamino-m-xylene. White needles recrystallized from gracial acetic acid. Yield 74%, mp 285-287° (Lit.[18] mp 295° corr.). d) 4,6-Diacetamino-isophthalic acid. As no experimental details are cited[18] for the oxidation of the previous compound with potassium permanganate, the following procedure was applied. In a warm (90°) stirred suspension of 4,6-diacetamino-m-xylene (0.1 mol) in 1 lt of water containing magnesium sulfate hydrate (0.125 mol), potassium permanganate (0.44 mol) were added in small parts after each disappearance of the colour of the solution. After 3hrs of reaction the warm discolored mixture was filtrated and the precipitated on cooling unreacted starting material was removed. Acidification of the warm filtrate with acetic acid afforded after cooling crystals of 4,6-diacetamino-isophthalic acid. Colourless needles recrystallized from alcohol (slight soluble in alcohol and hot water). Yield 40%, mp 265° dec. to red brown product (probably benz-bis-acetylanthranyl formed by intramolecular dehydration) (Lit.[18] mp 276° dec. corr., yield is not reported). e) Hydrolysis of diacetamino-isophthalic acid (0,1 mol) in conc. hydrochloric acid (800 ml) after boiling for 30 min and cooling yielded yellowish needles of the hydrochloric salt. The salt was readily hydrolized by treating with water and free 4,6-diamino-isophthalic acid was received as pinkish powder (mp 215-220°). This was purified by dissolving in a solution of sodium carbonate, treating with active carbon and precipitating by acidification with acetic acid. Colourles powder with triboelectric property. Yield 75%, mp 226-227° (Lit.[18] pinkish powder mp 235° corr.).

The ir spectrum showed absorption bands at 3495, 3375 cm^{-1} (NH), 1675 cm^{-1} (C=0) and at 1640 and 1615 cm^{-1}. The elemental analysis was in concordance with the formula.

Calcd for $C_8H_8N_2O_4$: C, 48,97; H, 4.08; N, 14.28%
Found: C, 48.92; H, 4.03; N, 14.46%

2,5-Diaminoterephtalic acid. It was prepared by a direct method[23] from pyromellitimide, mainting the reaction with the sodium azide at 50°C. The crude product (mp 320° dec.) was furthermore purified like the previous acid, as well as via its hydrochloric salt and finally by dissolving the free compound in hydrochloric acid, treating with active carbon and precipitating with ammonium hydroxide. Yellow green powder dried in vacuum. Yield 44%, mp 345° dec. (Lit. mp[23] $>300°$, mp[24] $>360°$, mp[25] $>400°$).

The ir spectrum showed a strong amine stretching band at 3450 and 3340 cm^{-1}, a broad shoulder at 1710 cm^{-1}, and a band at 1655 and 1200 cm^{-1}.

Analysis: Calcd for $C_8H_8N_2O_4$: C, 48.97; H, 4.08; N, 14.28%
Found: C, 48.66; H, 4.16; N, 14.13%

Polymerizations

1. Polyamic-acid III. [Poly-N-N'-(furan dicarbonyl-2")-3,3'-benzidinedicarboxylic acid].

A) Solution Polymerization. In a four-necked reaction vessel equipped with stirrer, thermometer, nitrogen inlet and outlet tube with calcium chloride and heated previously in order to remove any moisture in the apparatus, 5.44 g (0.02 mol) of purified 3,3'-dicarboxybenzidine (II) in 187 ml of dried (distilled over calcium hydride) N-methylpyrrolidone-2 containing 1.7 g (0.04 mol) of lithium chloride were dissolved with stirring and a thin stream of nitrogen. 3.94 (0.0204 mol) of freshly recrystallized 2,5-furan-dicarboxylic acid chloride (I) were added into the room temperature solution, with rapid stirring (Initial monomer concentration 5%). An exothermic reaction took place after a few minutes (3 min.) and a yellow pulpy solution was formed. Then it was heated at 120° for 20 min, and the viscous solution was quenched by pouring into water. The yellow precipitated polymer was separated by centrifugation and filtration in a sintered glass funnel and washed many times with warm distilled water until chlorine ions were not detected in the washings. Finally it was washed with methanol, drained by suction and dried in vacuum at 80° for 24 hrs. Yellowish brown powder. Yield 7.2 g (91.8%). The polymer did not melt below 365°. Inherent viscosity 0.61.

Analysis: Calcd for $(C_{20}H_{12}N_2O_7)_n$:	C, 61.24;	H, 3.06;	N, 7.14%
Found:	C, 59.18;	H, 3.27;	N, 6.92%

The ir spectrum in a potassium bromide disk or a nujol mull showed strong carbonyl stretching band of an amide group at 1675 cm.$^{-1}$

The polyamic-acid III is soluble (0.1 g/2 ml) in N-methylpyrrolidone-2 (NMP), dimethylacetamide (DMA), dimethylsulfoxide (DMS) containing lithium chloride, conc. sulfuric acid and in a mixture (1:1) of hexamethylphosphoramide (HMP) and NMP. It is insoluble in formamide, dimethylformamide (DMF) and HMP all containing lithium chloride and in a sodium hydroxide solution.

B) Interfacial polycondensation. In a polymerization vessel equipped with stirrer and nitrogen inlet 2.72 g (0.01 mol) of II in exactly 20 ml of 1N solution of sodium hydroxide (0.02 mol) and 20 ml of distilled water were dissolved. In the solution 0.2 g of sodium lauryl sulfate (Duponol), as surface active agent, and 4 g of sodium chloride to reduce the hydrolysis[26] of the chloride I were added. The solution was cooled to 0° and by vigorous agitation a cool solution of 2.03 g (0.0105 mol) of I in 40 ml of dried chloroform was added (The chloroform used was washed with water to insure removal of alcohol added as a stabilizer and dried over calcium hydride). Immediately a yellow polymer was obtained and agitation continued at 0° for 30 min. The emulsion was poured into acetone to coagulate the polymer and extract the solvents. The polymer was collected by filtration, washed thoroughly with warm water and finally with methanol and dried in vacuum (2 mm Hg) at 90° for 24 hrs. Yellow powder. Inherent viscosity 0.22.

The ir spectrum of the thus obtained polyamic-acid showed the presence of unreacted II. The latter was isolated, by treating the polymer with dilute hydrochloric acid and basifying the filtrate with sodium carbonate, and then was identified from its ir spectrum and that of an authentic sample of II. The finally purified polyamic-acid III showed inherent viscosity 0.27. Yield 3.2 g (80%).

2. Polybenzoxazinone IV. [Poly-2,2'-(furylene-2",5") -6,6'-bis-(4H-3, 1-benzoxazinone-4)].

In a small round flask 1.568 g (0.004 mol) of polyamic-acid III prepared by the solution polymerization procedure 1A were heated in a salt bath at 300° for 5 hrs under vacuum (1 mm Hg).

After cooling a weight loss of 12.2%, instead of the theoretical weight loss 9.18%, for the conversion of III to IV was found. Brown powder, inherent viscosity 0.66. The polymer did not melt up to 365°C.

Analysis: Calcd for $(C_{20}H_8N_2O_5)_n$:	C, 67.43;	H, 2.24;	N, 7.86%
Found:	C, 65.59;	H, 2.65;	N, 7.54%

The ir spectrum showed new characteristic absorption bands for the benzoxazinone[8] ring at 1760 cm^{-1} (ester carbonyl) and 1625 cm^{-1} (C = N) and the disappearence of the amide absorption band at 1675 cm.$^{-1}$

The polybenzoxazinone IV was insoluble in most tested organic solvents but soluble in conc. sulfuric acid.

3. Polyamic-acid V. [Poly-N,N-(furan dicarbonyl-2′,5′) -4,6-diamino-isophthalic acid].

A) Similarly to the procedure 1A, using 0.01 mol of 4,6-diamino-isophthalic acid and an initial monomer concentration 8%, a yellowish brown powder was obtained from the non viscous reaction solution. Yield (2.8 g 76%), the product did not melt up to 365° but changed colour. Inherent viscosity 0.07.

Analysis: Calcd for $(C_{14}H_8N_2O_7)_n$:	C, 53.16;	H, 2.53;	N, 8.86%
Found:	C, 50.25;	H, 3.39;	N, 7.86%

The ir spectrum of the nujol mull showed absorption bands at 3440 and 3340 cm^{-1} (NH), a broad band at 1690 cm^{-1} (carboxyl) and a shoulder at 1680 cm^{-1} (amide carbonyl).

B) The above procedure was repeated in low temperature in order to obtain higher value for the inherent viscosity[17,28] of the product. The reaction was carried out at -25°C for 30 min and subsequently at room temperature (22°) for 6 hrs. The inherent viscosity of the product obtained was again the same (0.07) as well as after an additional heating of the reaction solution at 120-130° for 3 hrs.

The yield and ir spectrum of the product were the same as those of the previous procedure 3A. The product (C, 49.88; H, 3.47; N, 8.57%) was partly soluble in a solution of sodium carbonate but no unreacted starting material was isolated from this.

C) Interfacial polycondensation. It was carried out using a pair of immiscible organic solvents.[29] Thus, 1.96 g (0.01 mol) of 4,6-diamino-isophthalic acid and 0.8 g (0.02 mol) of lithium chloride were dissolved in 60 ml of dried NMP and the solution cooled to 0°. A solution of 1.97 g (0.0102 mol) of I in 60 ml of dried hexane was added with vigorous stirring and a thin stream of nitrogen. Immediately a yellow colour appeared. The ice bath was removed after 10 min. and the emulsion was slowly heated at 165° by simultaneous distilling of hexane. The resultant solution was maintained at 165° for 6 hrs. A yellowish brown powder was obtained by the usual process. The inherent viscosity of the product was 0.07 in conc. sulfuric acid and 0.12 in NMP (0.5%, 25°). The yield and ir spectrum were also the same as those of the above procedures A and B.

4. Polybenz-bis (oxazinone) VII. [Poly-2,8-(furylene-2,′5′) -benz (a, δ) -bis (4H, 6H-3, 7, 1, 9, -oxazinone-4,6)].

The polyamic-acid obtained from the procedure 3A was heated in a round flask in vacuum (3 mm Hg) at 260° for 2 hrs and afterwards at 300° for 3 hrs. After cooling a weight loss of 30.1%, instead of the theoretical 11.3% for the conversion of VI to VII, was found. Brown powder. It did not melt up to 365°. Inherent viscosity 0.14.

Analysis: Calcd for $(C_{14}H_4N_2O_5)_n$:	C, 58.45;	H, 1.40;	N, 9.8%
Found:	C, 58.53;	H, 3.24;	N, 11.0%

The ir spectrum of the nujol mulls showed the characteristic absorption band for the benzoxazinone[8] ring at 1760 cm^{-1} but also a broad band at 1680 cm.$^{-1}$

5. Polyamic-acid VI. [Poly-N,N′-(furan dicarbonyl-2′,5′)-2,5-diaminoterephthalic acid].

A) Similarly to procedure 1A but using 2,5-diaminoterephthalic acid, an initial monomer concentration 4% in dried NMP (determined moisture content by K. Fischer method 0.02%) and a reaction temperature 0° for 30 min., followed by 1 hr at room temperature and finally 2 hrs at 120-130°, a green brown powder was obtained. Yield 55%. The product did not melt up to 365°. Inherent viscosity 0.07.

B) In a similar manner as procedure 3C, by using 2,5-diaminoterephthalic acid, 100 ml of both solvents and a final reaction temperature 180° for 7 hrs, a brown powder was obtained. Yield 79%. The product did not melt up to 365°. Inherent viscosity 0.08.

The ir spectrum showed a broad band at 1675 cm^{-1} (amide I) and for a heated sample used for the determination of melting point up to 365°, showed a broad band at 1760 cm^{-1} (ester carbonyl of benzoxazinone[8] ring).

A further study of the product was considered unimportant because of its very low inherent viscosity, prejudging poor properties.

Results and Discussion

A study of the reaction variables for the solution polymerization of II (proc. 1A), showed that the inherent viscosity of the polyamic-acid III formed in 5 min. from the begining of the reaction was 0.53 and after heating at 120° for twenty minutes it was increased to 0.61. Extention of the heating for an additional time for 2, 4 and 5 hrs did not change the extent of the polymerization and the inherent viscosity of the polymer obtained was the same.

Experiments for the effect of the initial monomer concentration (I + II/solvent W/V %) on the extent of polymerization showed that an initial monomer concentration of 11% was too high to give a homogenous reaction solution. Polymerizations with an initial monomer concentration of 6% and 7% afforded polymers with somewhat higher inherent viscosity (0.62 and 0.65 correspondingly) in respect to that of 5% (0.61).

Brittle brown transparent films were obtained from a solution of polyamic-acid III in N-methylpyrrolidone-2 dried (1 hr, 120°) onto glass plates.

The TGA thermogram for the polyamic-acid III showed a 3% loss of weight at 100-200°. This loss must be due to water of hydration which is removed at elevated temperature since heterocyclic polymers are frequently hygroscopic.[30] This absorbed water must be the cause of the corresponding lower carbon and nitrogen content of the product III found by the elemental analysis.

The DTA thermogram for III showed an endothermic inflection at 200°. At this temperature intramolecular cyclodehydration takes place by formation of polybenzoxazinone[8] ring, as it was confirmed by infrared spectrum.

The interfacial polycondensation of I with II (proc. 1B) afforded polyamic-acid III with a lower inherent viscosity (0.22) and unreacted II was found as impurity. Extension of the reaction time for 2 and 5 hrs did not change the extent of polymerization as well when it was carried out at room temperature. The procedure for a double monomer concentration also yielded crude polymer (79%) with the same inherent viscosity, whereas by an analogous procedure with terephthaloyl chloride the production of the corresponding polymer with a high inherent viscosity is reported.[31] Therefore the low inherent viscosity of III obtained by interfacial polycondensation must be due to the hydrolysis of the chloride I and secondly to the insufficient basicity of the diamine II.

The TGA thermogram for the poly(furylene) benzoxazinone IV showed that decomposition of the polymer starts at 320° with a weight loss 10, 20, 30, 40 and 60% at 440, 492, 536, 608, and 796° correspondingly. It is evident that the prepared poly(furylene) benzoxazinone IV did not show as a high thermal stability as the corresponding poly(m-phenylene)benzoxazinone.[8] This and the thermal stability of the corresponding polybenzimidazoles[4] testify to the fact that such polymers with furan ring have inferior thermal stability than those with benzene ring.

All the procedures applied with 4,6-diamino-isophthalic acid to prepare the polyamic-acid V gave products with low inherent viscosity (0.07-0.08) and the results of elemental analysis were different and not in good agreement with those expected. Therefore it is obvious that an oligomer with low molecular weight was obtained.

The TGA and DTA for the open chain precursor V showed a 2.5% loss of weight at 100-200° and also an endothermic inflection at 200° due to cyclodehydration forming benzoxazinone rings, as these were confirmed by the ir spectrum.

The TGA thermogram for the thermal conversion product VII showed an inferior thermal stability with starting of decomposition at 310°.

The excess weight loss from the theoretical value during the thermal conversion of V (proc. 4) should be due to decarboxylation of the unreacted carboxylic groups, to volatility of certain products and to intermolecular dehydration reactions. The increased inherent viscosity (0.14) of the resultant product can be explained by the latter also two events.

The reason that not extensive polymerization occured with 4,6-diamino-isophthalic acid may be due rather to its inreactivity.[18] However, high polymers derived from this, by reaction with other dicarboxylic acid chlorides[29,32,33] are reported. Nevertheless the procedure 3C which was carried out analogous to one of these references[29] did not afford the polyamic-acid V with a high expected inherent viscosity.

Similarly the reason that extensive polymerization did not also accur with 2,5-diaminoterephthalic acid may be ascribed to the inreactivity of this compound than to an insufficient purity of the material used. In favor of the former the amino-groups of 2,5-diaminoterephtalic acid is reported to be exceedingly inert.[34] In addition, the low inherent viscosity (0.06) of the polymer obtained by self polycondensation in polyphosphoric acid of this compound,[24] is likely to be ascribed also to this cause, as 3,3′-dicarboxybenzidine (II) afforded by the same manner a polymer with comparatively higher inherent viscosity.[24] However, polymerization of 2,5-diaminoterephthalic acid with 4,6-dimethylisophthaloyl chloride, by an analogous procedure to 3 C, afforded[29] polymer with high inherent viscosity.

Finally, the fact that polymers with high inherent viscosity have not been obtained by reaction of 2,5-furandicarboxylic acid chloride (I) with 4,6-diamino-isophthalic acid or 2,5-diaminoterepthalic acid may be also due to the lesser suitability of this chloride to afford high polymers with these compounds, in respect to the other referred chlorides, on account of the induced and resonance effect. However a further investigation to confirm the lesser suitability of 2,5-furandicarboxylic acid as starting material to produce high polymers stable at high temperature, in comparison with other acids is still required.

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Περίληψις.

Πολυσυμπύκνωσις τοῦ χλωριδίου τοῦ 2,5-φουρανοδικαρβονικοῦ ὀξέος μὲ ἀρωματικὰ διαμινοδικαρβονικὰ ὀξέα.

Πρὸς παρασκευὴν νέων πολυ(φουρυλενο)βενζοξαζινονῶν, σταθερῶν εἰς ὑψηλὴν θερμοκρασίαν, ἐκτελοῦνται τεχνικαὶ πολυμερισμοῦ εἰς διάλυμα καὶ διαφασικοῦ πολυμερισμοῦ τοῦ χλωριδίου τοῦ 2,5-φουρανοδικαρβικοῦ ὀξέος μὲ ἀρωματικὰ διαμινοδικαρβονικὰ ὀξέα. Ἕνα νέο πολυμερές, πολυ(φουρυλενο)βενζοξαζινόνη, μὲ μετρίως καλὴ θερμικὴ σταθερότητα (320°), παρασκευάζεται εἰς δύο στάδια μὲ τὴν 3,3′-δικαρβοξυβενζιδίνη. Τὸ ἀρχικῶς παρασκευαζόμενον πολυαμικὸν ὀξὺ παρέχει ἐκ διαλύματός του κατὰ τὴν ξήρανσίν του ἐπὶ πλακός, καστανοῦ χρώματος διαφανῆ εὔθρυπτον μεμβράνην. Ἡ παρασκευὴ ἀντιστοίχων πολυμερῶν μὲ 4,6-διαμινοϊσοφθαλικὸν ἢ 2,5-διαμινοτερεφθαλικὸν ὀξὺ ἀποδεικνύεται ὀλιγότερον ἐπιτυχής. Τὰ αἴτια μὴ ἐκτενοῦς πολυμερισμοῦ μὲ τὰς ἑνώσεις αὐτὰς ἀποδίδονται μᾶλλον εἰς τὴν μειωμένην ἱκανότητα ἀντιδράσεως τῶν ἀμινοομάδων τῶν ἑνώσεων αὐτῶν καὶ τὴν μικροτέραν καταλληλότητα τοῦ χλωριδίου τοῦ φουρανοδικαρβονικοῦ ὀξέος, ὡς πρὸς τὰ χλωρίδια τῶν βενζοδικαρβονικῶν ὀξέων. Ἀναφέρονται αἱ μέθοδοι παρασκευῆς τῶν μονομερῶν μετὰ τροποποιήσεων καὶ σχολίων, αἱ συνθῆκαι πολυμερισμῶν μετὰ μελέτης μερικῶν μεταβλητῶν τῶν ἀντιδράσεων καὶ συζητοῦνται τὰ ἀποτελέσματα.

References and Notes

1 Segal, G.: *"High-Temperature Polymers"*, Dekker Inc., N.Y. (1967).
2 Korshak, V.: *"Heat-Resistant Polymers"*, Translated from Russian by Schmorak J., ed. 1969, Israel Program for Scientific Translations, Jerusalem (1971).
3 Heertjes, P. and Kok, G.: *Delft Progress Report, Ser. A.*, **1**, 59 (1974).
4 Vogel, H. and Marvel, C.: *J. Polym. Sci.*, **50**, 511 (1961).
5 Korshak, V., Izyneev, A. and Vdovina, L.: *Izv. Akad. Nauk. USSR Ser. Khim.*, 4, 772 (1966); *Chem. Abstr.*, **65**, 9029 (1966).
6 Braz, G., Kardash, I., Yakubonich, V., Myasnikova, G., Ardashnikov Y., Oleinik, A., Dravednikov, A. and Yakubonich, A.: *Vysokomol. Soedin 8*, **2**, 272 (1966); *Chem. Abstr.*, **64**, 16008 (1966).
7 Korshak, V., Teplyakov, M. and Maksimov, A.: *Vysokomol. Soedin Ser. B9*, **12**, 870 (1967); *Chem. Abstr.*, **68**, 59936 (1968).
8 Yoda, N., Ikeda, K., Kurihara, M., Toyama, S. and Nakanishi, R.: *J. Polym. Sci., A-1*, **5**, 2359 (1967).
9 Sörenson, W. and Cambell, T.: *"Preparative Methods of Polymer Chemistry"*, 2nd ed., p. 95, Interscience Publishers Inc., N.Y. (1968).
10 Vogel, H. and Marvel, C.: *J. Polym. Sci.*, **50**, 530 (1961).
11 Mndzhoian, A.: *"Synthesis of Heterocyclic Compounds"*, Translated by Stubbes, E., Vol. 1, p. 27, Consultants Bureau N.Y., Plenum Publ. Corp. (1969).
12 Andrisamo, R.: *Ann. Chim.* (Rome), **40**, 30 (1950); *Chem. Abstr.*, **45**, 7563 (1951); Ref. 11, p. 29.
13 Tundo, A.: *Boll. Sci. Fac. Chim. Ind.* Bologna, **14**, 63 (1956); *Chem. Abstr.*, **51**, 5748 (1959).
14 Fierz-David, H. and Blangey, L.: *"Grundlegende Operationen der Farbenchemie", 8e Aufl.*, S. 157, Springer Verlag, Wien, (1952).
15 Kurihara, M. and Yoda, N.: *Bull. Chem. Soc. Jap.*, **40**, 2429 (1967).
16 Yoda, N. and Kurihara, M.: *Japan, Pat.* **22,177** (1966); *Chem. Abstr.*, **66**, 65296 (1967).
17 Toyama, S., Ikeda, K., Kurihara, M. and Yoda, N.: *Japan. Pat.* **3,769** (1970); *Chem. Abstr.*, **73**, 14498 (1970).
18 Bogert, M. and Kropff, A.: *J. Amer. Chem. Soc.*, **31**, 843 (1909).
19 Nolting, E. and Collin, A.: *Ber.* **17**, 265 (1884).
20 Deilly, J. and O' Neill, B.: *J. Soc. Chem. Ind.*, **46**, 227 (1927).
21 Witt., O.: *Ber.*, **21**, 2419 (1888).
22 Morgan, G.: *J. Chem. Soc.*, **81**, 92 (1902).
23 Caronna, C. and Palazzo, S.: *Gaz. Chim. Ital.*, **94**, 809 (1964).

24 Kurihara, M.: *Makrom, Chem.*, **105**, 84 (1967); Yoda, N. and Kurihara, M.: *J. Polym. Sci., Part-D, "Macromolecular Reviews", 5, 109 (1971).*
25 *Errede, L.: U.S. Pat.* **3,408,326** (1968).
26 Morgan, P., and Kwolek, S.: *J. Polym. Sci.*, **40**, 299 (1959).
27 Iwakura, Y., Uno, K., Imai, Y. and Fukui, M.: *Makrom. Chem.*, **77**, 41 (1964).
28 Yoda, N., Kurihara, M. and Ikeda, K.: *Japan. Pat.* **15, 839** (1968); *Chem. Abstr.*, **70**, 20509 (1969).
29 Yoda, N., Nakanishi, R., Kubota, T., Kurihara, M. and Ikeda, K.: *Franc. Pat.* **1,448,897** (1966).
30 Conley, R.: *"Thermal Stability of Polymers"*, Vol. 1, p. 551, M. Dekker, N.Y. (1970).
31 Yoda, N., Kurihara, M. and Ikeda, K.: *Japan. Pat.* **27,633** (1968); *Chem. Abstr.*, **70**, 88451 (1969).
32 Hill, H., Kwolek, S. and Sweeny, W.: *U.S. Pat.* **3,380,969** (1968).
33 Yoda, N. and Kurihara, M.: *Japan. Pat.* **11,239** (1968); *Chem. Abstr.*, **70**, 4813 (1969).
34 Borget, M. and Box, A.: *J. Amer. Chem. Soc.*, **27**, 1137 (1905).

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POLAROGRAPHIC BEHAVIOR AND ACETAL FORMATION KINETICS OF p-SUBSTITUTED BENZALDEHYDES IN METHANOL

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Summary

The polarographic behavior of p-substituted benzaldehyde derivatives XC_6H_4CHO, where X = H, Cl, Br, F, CH_3, OCH_3, COOH, CN, CHO, $N(CH_3)_2$ and NO_2, in methanol in the absence as well as, after the addition of weak or strong proton donors is studied. The carbonyl group is reduced in two steps, except in the case of the presence of a strong electron releasing substituent, such as -$N(CH_3)_2$ or -NH_2, in the p- position of benzaldehyde molecule, in which case the carbonyl group undergoes an one-step reduction to the two electron level. Weak proton donors, such as benzoic acid, cause an easier uptake of the first electron, probably because of surface protonation of the depolarizer, so that a half-wave shift of the first reduction step towards more positive potentialvalues is observed. The addition of methanolic HCl in small amounts results in the formation of the corresponding dimethylacetal, the kinetics of which obeys the equation of first-order reactions. In the presence of water (1 - 6%v/v) for acetal formation holds sufficiently the equation of opposing first-order reactions and an equilibrium is established.

The half-wave potentials of carbonyl reduction as well as, the rate constants of acetal formation are correlated with Hammett's σ substituent constant. In case of polarographic reduction of carbonyl the σ^--value for -COOH and σ^+-value for -F fit the Hammett linear relationship of the rest substituents and the reaction constant has been found $\varrho_\pi = 0.325 \pm 0.006$. In case of acetal formation the σ^--value for -NO_2 and the σ^+-value for -F fit the Hammett equation and the reaction constant has been found $\varrho_R = -1.68 \pm 0.06$.

Key words: Weak and strong proton donors, Rate constant, Equilibrium, Substituent effect, Hammett equation, Reaction constant.

Introduction

After the studies which have been carried out on the influence of proton donors upon the polarographic behavior of nitro-, nitroso- and azocompounds in aprotic or poor protic solvents,[1-3] it was decided to investigate systematically the influence of proton donors on the polarographic behavior of aromatic aldehydes in the same kind of solvents. When benzaldehyde was used as the depolarizer in the absence of proton donors, it has been observed that its polarographic reduction took place in two one-electron steps.[4] The limiting current has been found to be, diffusion controlled and the wave-heights proportional to the benzaldehyde concentration.

After the addition of proton donors, which are practically undissociated in methanol, i.e. benzoic acid, the shape of the whole polarographic curve and probably the reduction of aldehyde group have remained substantially unchanged.

Only a relative small shift (about 0.06 Volts) of half wave potential of the first reduction step to more positive potential values has been observed. These methanolic solutions of benzaldehyde, as well as that of nitrobenzaldehydes, have remained constant, in what concerns the place and the heights of waves, even after 12 hours from the preparation.

When methanolic solution of HCl of the same or slightly smaller concentration to that of depolarizer has been added, the polarographic reduction waves of aldehyde group have disappeared even after the small time of mixing and taking the polarogram (about 3 min.). However, when the HCl-concentration was at least ten times smaller than that of benzaldehyde, a decrease of the wave-height, corresponding to the polarographic reduction of aldehyde group, has been observed with time, until the wave-height became practically equal to zero. This has been attributed to the conversion of the aldehydes to their dimethylacetals. Anyhow, it is due to the conversion of the aldehyde group to a polarographically inactive group (hemiacetal or acetal).

From the decreasing rate of the wave-height has been assumed that under the experimental conditions the above conversion can be described with a first-order kinetic equation. The rate constant value of this reaction depends on the HCl-concentration in solution and varies linearly with it.

In the present work we have extended our study to other p-substituted derivatives of benzaldehyde in order to strengthen our initial assumption that at the dropping mercury electrode both the free aldehyde and hemiacetal are electroreduced and that the polarographic inactive product is the acetal.

Another subject of this work is to study what is in general the effect of various substituents. Studing the polarographic reduction of benzaldehyde and its substituted derivatives in methanol as well as with the addition of small amounts of HCl there is a possibility to observe the effect of substituents both on heterogeneous reaction of the polarographic reduction of carbonyl group, as well as on the reaction rate of acetal formation in bulk solution.

Experimental

Polarographic curves as well as the values of diffusion current during the kinetic studies have been taken with a Radiometer polarograph "Polariter PO4". Reduction potential values were taken in reference to the aqueous saturated calomel electrode (S.C.E.). The polarographic cell used and further experimental details have been discribed elsewhere.[4-6] The cell and solutions have been kept always in waterbath of constant temperature 25±0.1°C. The concentration of aldehydes was 10^{-3} M and that of HCl 10^{-4} M in the solutions under investigation except otherwise stated. As supporting electrolyte has been used LiCl 0.1 M in the final solutions. The time began to be measured after the half volume of HCl-solution has been added into the methanol solution of aldehyde.

The substances used were Benzaldehyde R.P., p-dimethylaminobenzaldehyde P. and lithium chloride R.P. from Carlo-Erba, p-nitrobenzaldehyde p.a., p-chlorobenzaldehyde p.a., p-bromobenzaldehyde p., p-methylbenzaldehyde p., p-methoxybenzaldehyde and terephthalaldehyde from Fluka, p-fluorobenzaldehyde and p-carboxybenzaldehyde from Koch-Light Lab. and methanol "zur analyse" from Merck. p-cyanobenzaldehyde has been prepared from p-cyanotoluene according to the method of Lieberman and Connor.[7] Its m.p. has been found to be 98-99°C and its purity has been checked by thin layer chromatography and IR spectrum.

Results and discussion

a. Polarographic reduction in absence and/or presence of weak proton donors.

The polarographic study of p-substituted benzaldehyde derivatives under examination has shown that the reduction of aldehyde group at d.m.e. in methanol solutions proceeds, except in cases of p-dimethylaminobenzaldehyde, p-nitrobenzaldehyde and terephthalaldehyde, in two steps as that has been observed by the polarographic reduction of benzaldehyde.[4] The wave-heights (i_1 and i_2) of these two steps are almost equal and they correspond to the uptake of one electron to each step. This came out from comparison of the wave-heights to that of the nitrobenzene reduction in methanol under the same conditions. They vary proportionally with the change of aldehyde concentration in the solution. The polarographic curves are shown in Fig. 1, where the curve of benzaldehyde has been also placed for comparison purposes. In this figure the polarographic curve of p-nitrobenzaldehyde has been omitted, since it has been given and commented elsewhere.[4,5]

Comparing the waves of aldehydes of different kind but of the same concentration, they have been found to possess equal heights. Slight deviations are attributed to the change of diffusion coefficients. This observation - also having in mind that the equilibrium aldehyde = hemiacetal is shifted less or more towards the

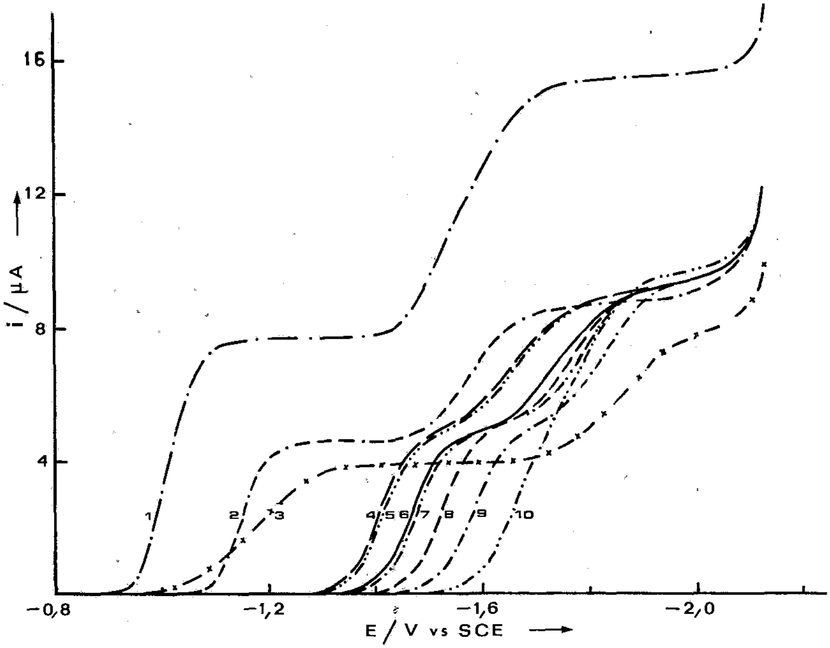


FIG. 1. *Polarographic curves of benzaldehyde and its p-substituted derivatives* $X\text{-}C_6H_4CHO$ *(10^{-3} M) in methanol:* X is: 1) -CHO, 2) -CN, 3) -COOH, 4) -Br, 5) -Cl, 6) -H, 7) -F, 8) $-CH_3$, 9) $-OCH_3$, 10) $-N(CH_3)_2$. Supporting electrolyte LiCl 0,1 M.

hemiacetal side depending on the nature of substituent[8-10] - forces us to accept that both the free aldehyde-form and the hemiacetal amount present in equilibrium with it are reducible at the d.m.e. Because of the electroreduction of aldehyde-form the equilibrium between these two forms is disturbed, at least on the electrode surface and the hemiacetal-form present is converted rapidly to reducible aldehyde-form.

After the addition of weak proton donors, such as benzoic acid, the following polarographic behavior has been observed:

When the concentration of added proton donor is smaller than that of depolarizer the first of the one-electron waves is separated in two steps, the first of which is shifted towards more positive potential values. So a prewave appears and the polarogram seems as a three-wave polarographic curve. The heights (i'_1 and i'_2) of these first two steps have a sum equal to the height ($i'_3 = i_2$) of the third one-electron wave, which remains at the same position and has the same height as that of the second step in the case of reduction without addition of any proton donor. The height ratio, i'_1/i'_2, is equal to the ratio of the molecular concentrations of proton donor and depolarizer in solution. The heights sum, $i'_1+i'_2$, is equal to i_1 and the position of i'_2 is the same as that of i_1.

As has been already mentioned, the height of prewave (i'_1) is proportional to the donor concentration and is varied regularly by changing the donor concentration until it becomes equal to that of the depolarizer. When the proton donor concentration is equal to that of the depolarizer the first one-electron wave appears in the position of the prewave and i'_1 is equal to i_1. The polarograms have then the form of those without addition of proton donor with their first wave (addition of the first electron) shifted towards more positive potentials. The second wave, which corresponds to the addition of the second electron, remains in both cases, that is with or without addition of proton donor, at the same potential. The half-wave potential difference of the two waves for benzaldehyde and benzoic adic system is greater by 60 mV that it is in the case of the same depolarizer without any addition of proton donor. The wave-heights of the two waves are almost equal one to each other. The same polarographic behavior has been observed even if the proton donor concentration was twice as that of the depolarizer. Addition of proton donor in more than twice the previous concentration had as result the deformation of the polarographic curve and the no good separation of the waves between each other.

After that we cannot say that the first wave (i_1) is due to the reduction of a protonized form of aromatic aldehydes, as that occurs in the case of polarographic reduction of carbonyl compounds in acidic aqueous buffered solutions.[11] We attribute this wave to the formation of the radical anion ArCOH-, which is further reduced in more negative potentials probably with preceding protonation. The first of the steps (i'_1) to which the first one-electron wave is divided after the addition of proton donor, is attributed to the reduction of the part of carbonyl group protonated on the electrode surface, which results to the formation of free radical $ArCOH_2$. The second step (i'_2) is attributed to the reduction of the rest unprotonated form, because of the insufficiency of proton donor. This assumption agrees with the aspects of Mairanovskii for reduction of benzaldehyde in acidic media.[12] The fact that the half-wave potential of the free radical reduction is the same with that of the radical anion reduction is an evidence that the latest is protonated before its further reduction.

This polarographic behavior guides us to guess that carbonyl group of aromatic aldehydes in methanol solutions without the addition of proton donor is probably reduced according to the sequence: electron, proton, electron, proton (e, H^+, e, H^+). With addition of weak (almost undissociated) proton donors the reduction proceeds according to the sequence H^+, e, e, H^+, when the proton donor concentration is equal or greater to that of aldehyde. In this case the preprotonation in the bulk solution should be excluded and consequently it must be accepted that a surface protonation of carbonyl group takes place.[13] When the proton donor concentration is smaller than that of aldehyde, only a part of it, proportional to the donor concentration is reduced according to the above mechanism and so we observe the prewave, mentioned already. The rest of the aldehyde is reduced according to the mechanism in the absence of proton donor.

b. Substituent effect on the half-wave potential.

The substitution in the p-position in the molecule of benzaldehyde has not influenced basically the form of polarographic curves except of the half-wave potential values of two reduction steps of aldehyde group. Consequently, we can accept the same reduction procedures in the case of p-substituted benzaldehyde derivatives as that of benzaldehyde. The substituent influence is more pronounced mainly during the first step, that is on the uptake of the first electron. The produced shift of the first reduction step towards more positive or more negative potential values depends mainly on the electronegative or electropositive character of the individual substituent. These substituents, which cause a decrease of electron density to the aldehyde group with their inductive and mesomeric effects, produce a shift towards more positive potential values. On the contrary, these substituents, which cause an electron density increase to the aldehyde carbonyl, such as dimethylamin-group, produce a shift towards more negative potential values. As a result of this negative shift, it is possible the uptake of the first electron to be followed immediately by the uptake of a second electron. In this case a two-electron polarographic wave is observed (Fig. 1 curve 10). A similar wave for the carbonyl group reduction has been also observed in the case of p-nitrobenzaldehyde.[4] Although nitrogroup itself is an electron withdrawing group its reduction product (amine group) is an electron releasing group. In the case of p-nitrobenzaldehyde the electroreduction of nitro group at the d.m.e. is completed to more positive potential values than that of carbonyl group.[4,14,15] Therefore, the reduction of carbonyl group takes place in this case not under the influence of nitro group but under the influence of its reduction product.

In the case of terephthalaldehyde a double polarographic wave is obtained. The height of each individual wave corresponds to the uptake of two electrons (Fig. 1 curve 1). However, we are not able, at the moment , to state if the first of these waves corresponds to the full reduction of one carbonyl group or to the reduction by one electron of both carbonyl groups of depolarizer.

Generally, substituents causing a positive shift to the first wave cause an also positive shift and to the second one. However, in the case of p-carboxybenzaldehyde a negative shift for the second wave has been observed, the same substituent causes a positive shift to the first wave (Fig. 1, curve 3). To this the following explanation could be given. Since carboxyl group offers its proton during the first reduction step, the further reduction proceeds under the influence of anionic carboxylat group.

Quantitative expression of the substituent effect on a reaction is the Hammett equation, which in the case of a polarographic process takes the form[16]

$$(E_{1/2})_x - (E_{1/2})_o = (\Delta E_{1/2})_x = \varrho_\pi \sigma_x, \qquad (1)$$

where $(E_{1/2})_o$ is the half-wave potential of unsubstituted substance and $(E_{1/2})_x$ the half-wave potential of the compound containing the substituent X.

On the basis of half-wave potential values of the first reduction step for benzaldehyde and its p-substituted derivatives in pure methanol and the σ_x substituent's constant values, taken from the literature cited,[16,17] the diagram of figure 2 is obtained.

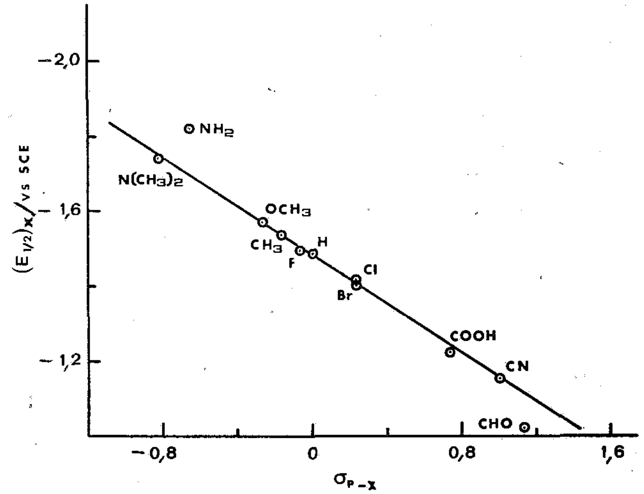
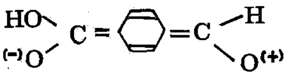


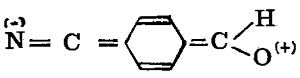
FIG. 2. *Dependence of $E_{1/2}$ of p-substituted benzaldehydes on substituent constant σ-values.*

The half -wave potentials of the two-electrons polarographic waves have been assumed as $(E_{1/2})_x$ values in cases of p-dimethylaminobenzaldehyde and terephthalaldehyde. In case of p-carboxybenzaldehyde it has been also taken in account that the observed half-wave potential shift of the first reduction step, equal to +0.320 Volts, is the result of two effects. These are the decrease of electron density of aldehyde group under the influence of inductive and mesomeric effects of carboxyl group and the simultaneous action of this substituent as a weak proton donor. Considering that the strength of carboxyl group of p-carboxybenzaldehyde in methanol is of the same magnitude order as that of benzoic acid, causing to the first reduction step of benzaldehyde a shift equal to +0.060 Volts, this amount has been used as correction to calculate the halfwave potential of aldehyde group reduction under the influence of inductive and mesomeric effects of carboxyl group. So the corrected value $(E_{1/2})_{COOH} = -1.165-0.060 = -1.225$ V.vs S.C.E. has been considered.

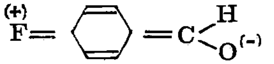
For the substituents -COOH, -CN and -CHO different σ_x values are given in the bibliography,[16-19] meaning that these substituents act on the reaction center in a different way, depending on the kind of the reaction under investigation. In this paper as σ_x values for these substituents the σ^-_{p-x} values (+0.73, +1.00 and +1.13)[16] have been adopted as more representative so long as, a considerable mesomeric interaction between the reactive group and the substituent can occur via the benzene ring.[16,18] Values of σ^-_{p-x} were also used for correlation of half-wave potentials for benzaldehydes by Grabowski in buffered solutions of pH 13.[16b] For the corresponding substances in our case, contributions due to resonance structures, such as



and



ought to be significant. For similar reason the value $\sigma^{+}_{p\text{-}x} = -0.07$[16] has been considered as value of σ_x for fluor atom, because of the resonance structure



Similar hehavior of fluor atom has been observed in the case of polarographic reduction of p-fluoronitrobenzene in methanol.[6]

After that a very satisfactory linear dependence of $(E_{1/2})_x$ on σ_x values has been observed, as it is shown in Fig. 2. Slight deviations from linearity have been observed for substituents $-NH_2$ and -CHO. These could be also attributed to mesomeric interactions because of resonance structures similar to that given for p-fluorobenzaldehyde, or to reduction mechanism, especially in case of terephthalaldehyde, since its first wave, whose the $E_{1/2}$ value has been considered to determine the substituent effect, may be due to the reduction by one electron of both aldehyde groups of depolarizer.

Exlcuding these two deviating compounds and using the correlation method describing by Jaffé[18] for reaction constant is obtained the value $\varrho_\pi = 0.325 \pm 0.006$ with standard deviation $s = 0.010$ and correlation coefficient $r = 0.998$. Using this value for ϱ_π and the half-wave potentials for the first reduction wave of p-aminobenzaldehyde and terephthalaldehyde the values -1.05 and +1.40 result as σ-values for substituents $-NH_2$ and -CHO respectively.

The found reaction constant value is equal to that reported for the polarographic reduction of substituted banzaldehydes by a nucleophilic mechanism in aqueous buffered solutions.[16] Its positive sign indicates that the reaction is facilitated by a low electron density at the reaction center.

c. Behavior in the presence of strong proton donor.

The addition of methanol solution of HCl into methanol solutions of benzaldehyde or some of its p-substituted derivatives in almost equimolar quantities (10^{-3} M) has as result the disappearance of the wave corresponding to the reduction of carbonyl group. When the final concentration of HCl is 10^{-4} M or less a regular decrease of height with time for both the two waves of aldehyde group polarographic reduction curves is observed. This is shown in the case of p-cyanobenzaldehyde, as an example, in Fig. 3.

This fact is attributed to the conversion of aldehyde via hemiacetal to the corresponding dimethylacetal. This conversion is catalysed by the $CH_3OH_2^+$ present. The conversion, under the experimental conditions, is practically quantitative as gathered from final nullification of the wave-heights in all cases. A similar wave-height decrease, observed during polarographic reduction of the protonized form of benzaldehyde in ethanol buffered solutions (pH<5) by Laviron and Lucy, has been also attributed to the acetal formation.[20]

The formation of hemiacetals obeys to first order kinetics and is subject to general acid and general base catalysis, while acetal formation from mixtures of carbonyl compounds and alcohols takes place in the presence, even of traces, of strong proton donors.[21] No sensible wave-height decrease has been observed in

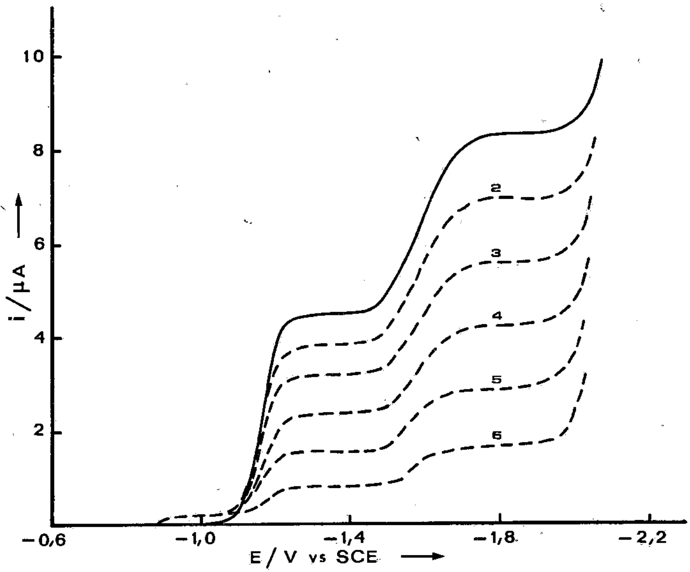


FIG. 3. *Polarographic curves of p-CNC_6H_4CHO of initial concentration 10^{-3} M in methanol in the presence of 10^{-4} M HCl at different time intervals in hours:* 1) 0,0 without HCl, 2) 3,5, 3) 8,5, 4) 15,5, 5) 24,3 6) 40,3 hours. Supporting electrolyte LiCl 0,1 M.

neutral methanol solutions of aldehydes at least for a period of 24 hours even after the addition of small amounts of LiOH-methanol solution. After that we have attributed the decrease of wave-heights with time in acid methanol solutions to acetal formation. Hemiacetal may be formed in significant amounts even after mixing,[22] although the use of ultraviolet spectrophotometry and of chemical methods has indicated that by most aromatic aldehydes the hemiacetal formation is very poor.[21] In any case, the addition of a catalyst, such as strong proton donors, has as result the formation of acetals with much smaller reaction rate than that of hemiacetal formation which enables the two reaction to be kinetically distinguished.[23] Since that the step of acetal formation is the rate determining one.

The reaction of acetal formation strictly examined is a bimolecular reaction. However, under the experimental conditions (mole ratio of aldehyde to methanol $\cong$ 1:25000) this reaction becomes a pseudomonomolecular one.

Since we have accepted that aldehyde and hemiacetal in equilibrium are reduced at the d.m.e., the diffusion current i_t after a time t from the moment of addition of H^+ will be a measure of their total concentration at this time. If i_o is the diffusion current at time null, the difference i_o - i_t will be then a measure of the amount of acetal, which has been formed at the time t. The logarithm of i_t is altered linearly with time, as it is shawn in Fig. 4.

This means that in fact the acetal formation follows the first order kinetic equation, which takes under the experimental conditions the following form:

$$k = \frac{2.303}{t} \log \frac{i_o}{i_t} \tag{1}$$

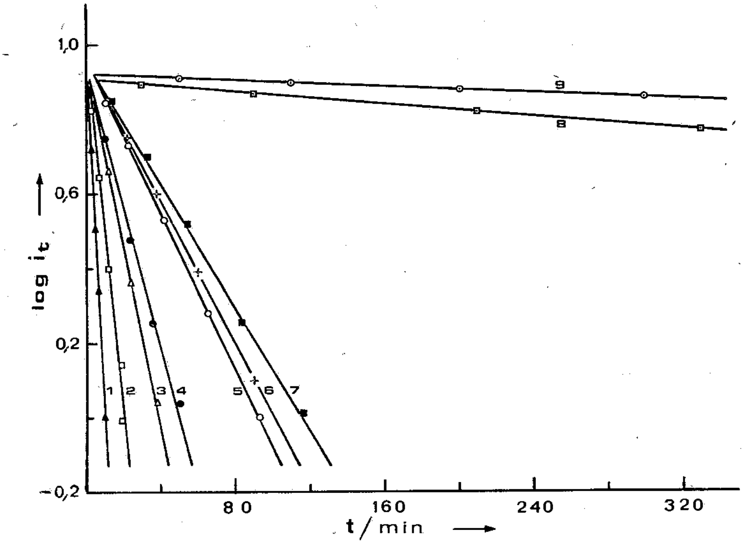


FIG. 4. *Dependence of logi$_t$ on time for p-substituted benzaldehyde derivatives of initial concentration 10^{-3} M in the presence of 10^{-4} M HCl:* 1) X = -OCH_3, 2) -CH_3, 3) -F, 4) -H, 5) -Cl, 6) -COOH, 7) -Br, 8) -CN, 9) -NO_2. Supporting electrolyte LiCl 0,1 M.

The calculated values of rate constant k depend on concentration of HCl and are varied linearly with it. Consequently, the reaction of acetal formation in methanol is a catalytic reaction catalyzed by $CH_3OH_2^+$, as that has also been observed earlier in cases of benzaldehyde[4] and p-nitrocinnamaldehyde.[5]

For the acetal formation rate constant k_x of benzaldehyde and its p-substituted derivatives in methanol and in the presence of HCl 10^{-4} M the values given in table I have been found polarographically from the slopes of curves of logi$_t$ against t.

The correlation of logk_x with σ-values of substituents has a result shown in the Fig. 5.

The experimental results in case of terephthalaldehyde appear as if the formation of corresponding acetal to be kinetically a consecutive reaction and this substance will be further investigated. In case also of p-dimethylaminobenzaldehyde the kinetics are very fast in presence of HCl concentration used in all other cases. Therefore these substances have not been considered.

As σ-values for substituents -CN and -NO_2 the $\sigma^-_{p\text{-}x}$ values +1.00 and +1.27 have been used, while for -F the $\sigma^+_{p\text{-}x}$ value -0.07 has been considered. Under these presuppositions and excluding the case of p-carboxybenzaldehyde a very good linear free energy relationship is obtained, as it is shown in Fig. 5. From this relationship the value $\varrho_R = -1.68 \pm 0.06$ is calculated for the reaction constant with a standard deviation $s = 0.096$ and correlation coefficient $r = 0.996$.

After that the value 0.218 results as σ-value for substituent p-COOH. This value is very close to that of 0.21 mentioned in the literature[16,18] as lower limit for p-COOH when this substituent acts mainly with its polar inductive effect.

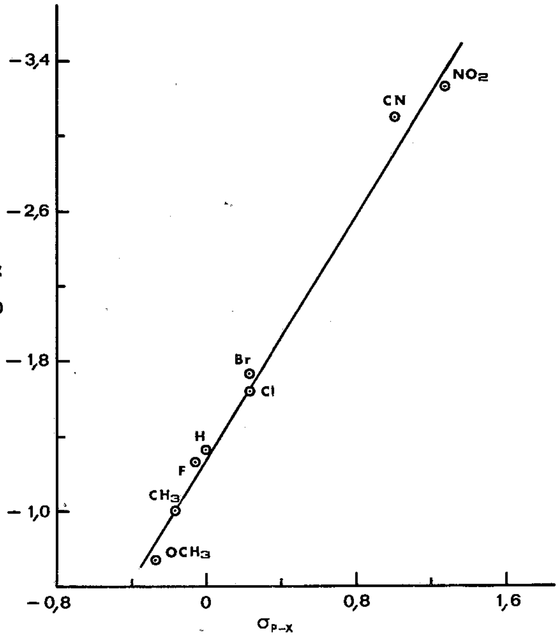


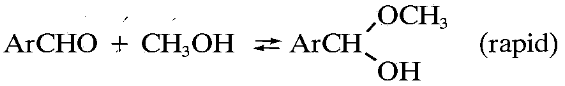
FIG. 5. *Relation of logk_x with σ_x -values for acetal formation of p-substituted benzaldehyde derivatives in methanol.*

TABLE I. *$E_{1/2}$ -values and rate constants for acetal formation of p-XC_6H_4CHO in MeOH. HCl 10^4 M, LiCl 0.1 M.*

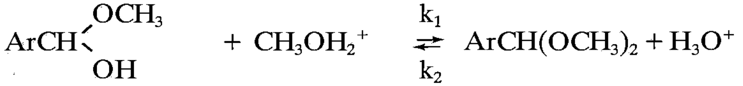
Substituent X	$(E_{1/2})_x$ Volt vs. SCE	$k_x \cdot 10^2$ min^{-1}	σ_x
H	$(E_{1/2})_o$ =-1.485	k_o = 4.60	
CH_3	-1.535	9.95	-0.170
OCH_3	-1.570	18.20	-0.268
Cl	-1.415	2.30	0.227
Br	-1.405	1.84	0.235
F	-1.490	5.34	-0.07
CN	-1.155	0.079	1.00
COOH	-1.225 (cor.)	2.16	0.73
CHO	-1.020	?	1.13
$N(CH_3)_2$	-1.740	fast	-0.83
NO_2	-	0.049	1.27
NH_2	-1.82	-	-0.66

From the substances studied already it is gathered that the substituents -CH_3, -OCH_3, -Cl, -Br, -F and -CN in p-position of benzaldehyde interact with the same mechanism both on the polarographic reduction of aromatic aldehyde group as well as on the conversion of aldehyde group, or better of hemiacetal group, to acetal. The substituent p-COOH acts in a different way in either case.

Substituents in p-position producing because of their character a half-wave shift of the aldehyde group reduction wave towards more positive potential values decrease the rate of acetal formation. On the contrary, these substituents which produce a half-wave shift to more negative potential values increase the rate of acetalization. This observation constitutes a confirmation for the mechanism of acetal formation



$$ArCHO + CH_3OH \rightleftharpoons ArCH\begin{matrix}OCH_3\\OH\end{matrix} \quad \text{(rapid)} \qquad I$$



$$ArCH\begin{matrix}OCH_3\\OH\end{matrix} + CH_3OH_2^+ \underset{k_2}{\overset{k_1}{\rightleftharpoons}} ArCH(OCH_3)_2 + H_3O^+ \qquad II$$

(rate determining step)

which we have proposed in case of benzaldehyde acetalization.[4] It must also be stated that hydroxonium and methoxonium ions are kept in equilibrium as

$$CH_3OH^+_2 + H_2O \rightleftharpoons CH_3OH + H_3O^+ . \qquad III$$

According to the reaction II the system should be brought to an equilibrium state because of hydrolysis of formed acetal, catalysed also by acids. However in the used solutions hydrolysis of acetal has not been observed since diffusion current reaches practically zero, in all stydied substances, which means that finally no appreciable amount of free aldehyde or its hemiacetal were present in the tested solutions. This can be explained as due to very small amounts of water formed and to the binding of this water with ions of supporting electrolyte (LiCl 0.1 M) forming their hydration state. After that no appreciable hydrolysis is observed.

However, with an extra addition of small water amounts (1 - 6% v/v) the system reaches indeed the provided equilibrium. In this case the diffusion current decreases with time, but with smaller rate and reaches finally to a limiting value depending on the water amount which has been added. The limiting value of diffusion current for a certain aldehyde is independed on the HCl concentration of the system. This shows that the system has been brought to an equilibrium state depending only on the water content of the mixture and on the kind of reacting partners, which finds an explaination accepting the process of the reaction II. Since the concentration of the added water is larger than that of acetal and because of the catalytic role of $CH_3OH_2^+$ the kinetic of acetal formation follows in this case satisfactoryly the equation of reversible first-order reactions

$$k_1 = \frac{x_e}{a.t} \; 2.303 \log \frac{x_e}{x_e - x} \qquad (2)$$

where a is the total concentration of aldehyde at t=0, x is the concentration of acetal formed after a time t and x_e is the concentration of acetal at equilibrium state.

Since the kinetics of the reaction are followed polarographically and the product of reaction is polarographically inactive the equation (2) takes the form:

$$k_1 = \frac{i_o - i_e}{t \cdot i_o} \, 2.303 \log \frac{i_o - i_e}{i_t - i_e} \qquad (3)$$

In this equation i_e means the limiting value of diffusion current after the equilibrium has been established, while the rest of the symbols have the same meaning given elsewhere in the text.

The rate constant k_1 is obtained from the slope of diagrams of the log $(i_t - i_e)$ vs. t. Such diagrams are shown in Fig. 6 for the case of benzaldehyde in methanol solutions in the presence of $2{,}5.10^{-4}$ M HCl and 0.1 M LiCl after the addition of different water amounts.

Similar behavior has been also observed with p-substituted benzaldehyde derivatives.

In table II the values of the rate constant (k_1) of acetal formation from benzaldehyde and methanol in presence of small water amounts but with different HCl concentrations are summerized.

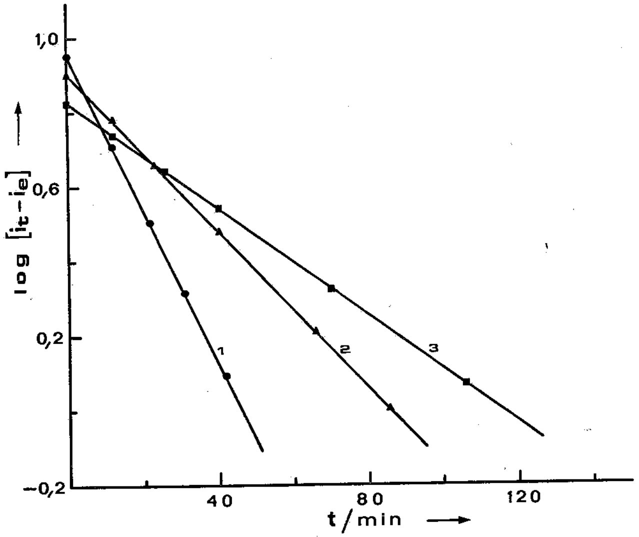


FIG. 6. *Dependence of log $(i_t - i_e)$ on time for benzaldehyde (in. conc. 10^{-3} M) in aqueous-methanol solutions in the presence of $2{,}5.10^{-4}$ M HCl:* 1) 2% v/v H_2O, 2) 4% v/v H_2O, 3) 6% v/v H_2O. Supporting electrolyte LiCl 0,1 M.

Increasing the water content, a regular decrease of rate constant has been observed. This is attributed to the decrease of activity of catalytically acting $CH_3OH_2^+$, because of the reaction III. This is also in agreement with the views of Deyrup.[24]

Significant decrease of rate constant has been also observed when small amounts of dimethylformamide have been added instead of water.

TABLE II. *Rate constants (k_1) of acetal formation of benzaldehyde in aqueous-methanol solutions (LiCl 0.1 M).*

Water content % v/v	HCl-concentration 1.10^{-4}	2.10^{-4}	$2.5\cdot10^{-4}$	3.10^{-4}	4.10^{-4}
1	$1.72\cdot10^{-2}$	—	—	—	—
2	$9.7\cdot10^{-3}$	—	$4.13\cdot10^{-2}$	—	—
4	$4.8\cdot10^{-3}$	—	$2.02\cdot10^{-2}$	—	—
6	$2.5\cdot10^{-3}$	$8.6\cdot10^{-3}$	$1.13\cdot10^{-2}$	$1.6\cdot10^{-2}$	$2.15\cdot10^{-2}$

In the case of methanol solution containing also small amounts of water the ratio $(i_o - i_e)/i_e$ is equal to the ratio [acetal]/([aldehyde]+[hemiacetal]) at the equilibrium state. This ratio, as it was expected, has been found depending on the water concentration but is independent from the HCl concentration. The same has also been observed during the investigation of acetalization of p-nitrocinnamaldehyde in methanol solutions.[5]

During our study on nitrobenzaldehydes in the presence of HCl and especially in the case of p-nitrobenzaldehyde, it has been observed that with the flow of time not only the wave-height corresponding to reduction of aldehyde group decreases, but also the wave corresponding to the first-step reduction of nitrogroup, lieing before that of aldehyde group, is divided in two parts.[4,5] The wave-heights of them vary with time but their sum remains constant and equal to the height of a four-electron polarographic wave. This differentiation of nitrogroup reduction-wave has been attributed to the change of substituent occuping a p-position relatively to nitrogroup. The first part of that double-wave has been attributed to the reduction of nitrogroup under the influence of aldehyde group, while the second one to the reduction of nitrogroup under the influence of aldehyde group conversion product, which is believed to be the dimethylacetal. We have decided to use this fact to verify our initial assumption that acetal is the polarographically inactive product, concerning the polarographic reduction of carbonyl, during the conversion of aldehyde group in methanol in the presence of HCl.

The dimethylacetal of p-nitrobenzaldehyde has been prepared according to the method proposed by Fischer and Giebe[25] and has been examined polarographically. The prepared substance has been purified by distillation under reduced pressure (b. p. 120-122 °C under 1 mmHg) and its purity has been checked with NMR spectroscopy. The signal area of methyl groups has been found exactly six times of that corresponding to methin hydrogen atom of group $-CH(OCH_3)_2$. The polarographic behavior of p-nitrobenzaldehyde-dimethylacetal has been found absolutely the same with that of the final product of the conversion of the p-nitrobenzaldehyde in methanol in the presence of small amounts of HCl.

All these, which have been extensively described in present paper persuade us that benzaldehyde and some of its simply p-substituted derivatives in methanol give after the addition small amounts of HCl as a final conversion product the corrsponding acetals. The kinetics of the conversion can be followed polarographically, because of the reduction at d.m.e. of aldehyde and hemiacetal, while the final product is polarographically inactive.

The σ-values for substituents $-CH_3$, $-OCH_3$, -Cl, -Br, -F(σ^+) and -CN(σ^-) in p-position fit the Hammett linear relation for both the heterogeneous reaction of polarographic reduction of carbonyl group, as well as for homogeneous reaction of acetal formation.

Περίληψις

Πολαρογραφικὴ συμπεριφορὰ καὶ κινητικὴ τοῦ σχηματισμοῦ ἀκετάλης τῶν π-ὑποκατεστημένων βενζαλδεϋδῶν ἐντὸς μεθανόλης

Μελετᾶται ἡ πολαρογραφικὴ ἀναγωγὴ π-ὑποκατεστημένων παραγώγων τῆς βενζαλδεῦδης τοῦ τύπου XC_6H_4CHO, ὅπου X = H, Cl, Br, F, CH_3, OCH_3, COOH, CHO, $N(CH_3)_2$ καὶ NO_2, ἐντὸς μεθανόλης, καθὼς καὶ ἡ ἐπίδρασις ἀσθενῶν καὶ ἰσχυρῶν δοτῶν πρωτονίων ἐπ' αὐτῆς.

Διαπιστοῦται ὅτι ἡ ἀναγωγὴ τῆς καρβονυλικῆς ὁμάδος λαμβάνει χώραν εἰς δύο στάδια (βαθμίδες) τοῦ ἑνὸς ἠλεκτρονίου, ἐκτὸς τῶν περιπτώσεων ἐκείνων κατὰ τὰς ὁποίας εἰς π-θέσιν τοῦ μορίου τῆς βενζαλδεῦδης εὑρίσκονται πυρηνόφιλοι ὑποκαταστάται, ὅπως π.χ. $N(CH_3)_2$ ἢ NH_2. Εἰς τὰς περιπτώσεις αὐτὰς ἡ πρώτη βαθμὶς ἀναγωγῆς μετατοπίζεται πρὸς ἀρνητικωτέρας τιμὰς δυναμικοῦ ἀκόμη καὶ μέχρις ἀλληλεπιθέσεως (ἐπικαλύψεως) τῶν δύο βαθμίδων, μὲ ἀποτέλεσμα ἡ πολαρογραφικὴ ἀναγωγὴ νὰ ἐμφανίζεται ὡς ἓν κῦμα δύο ἠλεκτρονίων.

Ἀσθενεῖς δόται πρωτονίων, ὅπως π.χ. τὸ βενζοϊκὸν ὀξύ, προκαλοῦν εὐκολωτέραν σχετικῶς πρόσληψιν τοῦ πρώτου ἠλεκτρονίου, λόγῳ πιθανῆς πρωτονιώσεως τοῦ ἀποπολωτοῦ ἐπὶ τῆς ἐπιφανείας τοῦ ἠλεκτροδίου μὲ ἀποτέλεσμα τὴν μετατόπισιν πρὸς θετικωτέρας τιμὰς δυναμικοῦ τῆς πρώτης βαθμίδος ἀναγωγῆς.

Διὰ τῆς προσθήκης HCl (εἰς τὰ μεθανολικὰ συστήματα) εἰς συγκεντρώσεις μικροτέρας ἐκείνης τῶν ἀποπολωτῶν παρατηρεῖται χρονικὴ ἐλάττωσις τοῦ ὕψους τοῦ κύματος ἀναγωγῆς τῆς καρβονυλικῆς ὁμάδος, πρᾶγμα τὸ ὁποῖον ἀποδίδεται εἰς τὸν σχηματισμὸν τῆς διμεθυλακετάλης μὲ ταχὺ ἐνδιάμεσο σχηματισμὸ τῆς ἡμιακετάλης. Ὁ σχηματισμὸς τῆς ἀκετάλης εἶναι τὸ καθορίζον στάδιον τὴν ταχύτητα τῆς ἀντιδράσεως, ἡ δὲ κινητικὴ αὐτοῦ, μελετωμένη πολαρογραφικῶς, ἀκολουθεῖ ἱκανοποιητικῶς τὴν ἐξίσωσιν τῶν ἀντιδράσεων πρώτης τάξεως. Μὲ τὴν προσθήκην μικρῶν ποσοτήτων ὕδατος (1 - 6% v/v) ἡ κινητικὴ τοῦ σχηματισμοῦ τῆς ἀκετάλης ἀκολουθεῖ τὴν ἐξίσωσιν τῶν ἀντιθέτων ἀντιδράσεων πρώτης τάξεως. Εἰς τὴν περίπτωσιν αὐτὴν ἀποκαθίσταται τελικῶς χαρακτηριστικὴ ἰσορροπία εἰς τὸ σύστημα, ἡ θέσις τῆς ὁποίας καθορίζεται, διὰ ὡρισμένην ἀλδεῦδην, ἀπὸ τὴν ποσότητα τοῦ προστιθεμένου ὕδατος, μόνον δὲ ἡ ταχύτης ἀποκαταστάσεως τῆς ἰσορροπίας ἐξαρτᾶται ἐκ τῆς συγκεντρώσεως τοῦ HCl εἰς τὸ διάλυμα.

Τὰ δυναμικὰ ἡμίσεως-κύματος τῆς ἀναγωγῆς τοῦ καρβονυλίου καθὼς καὶ αἱ σταθεραὶ ταχύτητος σχηματισμοῦ τῶν ἀκεταλῶν συσχετίζονται μὲ τὰς σταθερὰς ὑποκαταστατῶν σ (Hammett). Εἰς τὴν περίπτωσιν τῆς πολαρογραφικῆς ἀναγωγῆς τοῦ καρβονυλίου ἡ τιμὴ σ^- διὰ τὸ -COOH καὶ ἡ τιμὴ σ^+ διὰ τὸ -F ἐμπίπτουν εἰς τὴν γραμμικὴν σχέσιν τοῦ Hammett διὰ τοὺς ὑπολοίπους ὑποκαταστάτας. Ἡ σταθερὰ ἀντιδράσεως διὰ τὴν περίπτωσιν αὐτὴν εὑρέθη $\varrho_\pi = 0{,}325 \pm 0{,}006$. Διὰ τὴν περίπτωσιν τῆς ἀντιδράσεως σχηματισμοῦ ἀκετάλης ἡ τιμὴ σ^- διὰ τὴν NO_2-ὁμάδα καὶ ἡ τιμὴ σ^+ διὰ τὸ -F προσαρμόζονται ἐπιτυχῶς εἰς τὴν ἐξίσωσιν Hammett. Εἰς τὴν περίπτωσιν αὐτὴν διὰ τὴν σταθερὰν ἀντιδράσεως εὑρέθη ἡ τιμὴ $\varrho_R = -1{,}68 \pm 0{,}06$.

References and Notes

1 Jannakoudakis D. and Stalidis G.: *Chimika Chronika*, **32A**, 79 (1967).
2 Jannakoudakis D., Stalidis G. and Kokkinidis G.: *Sci. Annals Fac. Phys. & Mathem.* Univ. Thessaloniki, **11** 477 (1971).
3 Jannakoudakis D., Theodoridou E. and Kondoulis P.: *Sci. Annals Fac. Phys. and Mathem. Univ. Thessaloniki, 13,* 3 (1973).
4 Jannakoudakis D., Kokkinidis G. and Stalidis G.: *Sci. Annals Fac. Phys. and Mathem. Univ. Thessaloniki,* **11**, 523 (1971).
5 Jannakoudakis D., Stalidis G. and Kokkinidis G.: *Chimika Chronika, New Series,* **1**, 55 (1972).
6 Jannakoudakis D., Mavridis P.G. and Stalidis G.: *Chimika Chronika, New Series 3,* 1 (1974).
7 Lieberman S.V. and Connor R.: *Org. Synthesis,* **2**, 441.
8 Melchior N.C.: *J. Am. Chem. Soc.,* **71**, 3651 (1949).
9 Bell J.M., Kubler D.G., Sartwell P. and Zepp R.G.: *J. Org. Chem.,* **30**, 4284 (1965).
10 Mauser H. and Heitzer H.: *Z. Naturforsch,* **21b**, 109 (1966).
11 Zuman P., Barnes D. and Ryvolova-Kejharova A.: *Disc. Faraday Soc.,* **45**, 202 (1968).
12 Mairanovskii S.G.: *Talanta,* **12**, 1299 (1965).
13 Mairanovskii S.G.: *J. Electroanal. Chem.* **4**, 166 (1962).
14 Holleck L. and Marsen H.: *Z. Elektrochem.,* **57**, 944 (1953).
15 Day R.A. Jr. and Powers R.M.: *J. Am. Chem. Soc.,* **76**, 3085 (1954).
16 Zuman P.: *"Substituent effects in organic polarography"*, Ch. II: b), Ch III, p. 74 Plenum Press, New York (1967).
17 McDaniel D.H. and Brown H.C.: *J. Org. Chem.* **23**, 420 (1958).
18 Jaffé H.H.: *Chem. Rev.,* **53**, 191 (1953).
19 Hammett L.P.: *"Physical Organic Chemistry"* 2nd Ed. p. 356, McGraw-Hill, New York (1970).
20 Laviron E. and Lucy J-C.: *Bull. Soc. Chim.* (France), 2202 (1966).
21 Ogata Y. and Kawasaki A. in *"The chemistry of the carbonyl group"*, Vol. 2, pp. 16-17 (Edited by Zabicky J.), Intersience Publishers, London (1970).
22 Adkins H. and Broderich A.E.: *J. Am. Chem. Soc.,* **50**, 499 (1928).
23 Meadows G.W. and Darwent B. de B.: *Trans. Faraday Soc.* **48**, 1015 (1952).
24 Deyrup A.J.: *J. Am. Chem. Soc.,* **56**, 60 (1934).
25 Fischer E. and Giebe G.: *Ber.,* **30**, 3057 (1897).

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Η ΥΔΡΟΓΟΝΑΝΘΡΑΚΙΚΗ ΣΥΣΤΑΣΗ ΤΩΝ ΚΗΡΩΝ ΤΟΥ HYPERICUM PERFORATUM

ΒΑΣΙΛΕΙΟΣ Π. ΠΑΠΑΓΕΩΡΓΙΟΥ καὶ ΑΓΓΕΛΟΣ Ν. ΣΑΓΡΕΔΟΣ
Ἐργαστήριον Ὀργανικῆς Χημείας τῆς Πολυτεχνικῆς Σχολῆς τοῦ Ἀριστοτελείου Πανεπιστημίου Θεσσαλονίκης

(Ἐλήφθη τὴν 8η Σεπτεμβρίου 1976)

Στὴν ἐργασία αὐτὴ περιγράφεται ἡ ἀπομόνωση καὶ ἡ ταυτοποίηση τῶν ὑδρογονανθρακικῶν συστατικῶν τῶν κηρῶν τῆς φυτικῆς δρόγης Hypericum perforatum.[1,2]

Ἀπὸ τὴν ἔρευνα αὐτὴ προέκυψε ὅτι τὸ μίγμα τῶν κηρωδῶν συστατικῶν τοῦ φυτοῦ ἀποτελεῖται ἀπὸ ὑδρογονάνθρακες καὶ ἄλλα συστατικά, πιθανῶς ἐστέρες καὶ μεγαλομοριακὲς ἀλκοόλες, ἡ δομὴ τῶν ὁποίων δὲν διευκρινίστηκε ἀκόμη.

Τὸ ὑδρογονανθρακικὸ μέρος τοῦ παραπάνω μίγματος ἀποτελεῖται ἀπὸ ἕνδεκα ὑδρογονάνθρακες ποὺ περιέχουν ἀπὸ C_{21} ἕως C_{31}. Ὅλοι οἱ ὑδρογονάνθρακες εἶναι κορεσμένοι καὶ ἔχουν εὐθεία ἀνθρακικὴ ἁλυσίδα. Σὲ μεγαλύτερη ἀναλογία (~83%) ἀπαντᾶ ὁ ὑδρογονάνθρακας μὲ C_{29}. Ἀξιοσημείωτο εἶναι τὸ γεγονὸς ὅτι ἐμφανίζονται ὑδρογονάνθρακες μὲ περιττὸ καὶ ἄρτιο ἀριθμὸ ἀτόμων ἄνθρακος. Οἱ μὲ περιττὸ ἀριθμὸ ἀτόμων ἄνθρακος ἀπαντοῦν σὲ διπλάσια περίπου ἀναλογία (ἐκτὸς τοῦ C_{29} ποὺ ἀπαντᾶ σὲ πολλαπλάσια) ἀπὸ τοὺς ἀμέσως ἑπόμενους ἢ προηγούμενους μὲ ἄρτιο ἀριθμὸ ἀτόμων ἄνθρακος. Ἡ πορεία ποὺ ἀκολουθήθηκε εἶναι ἡ ἑξῆς:

Ὁλόκληρη ἡ δρόγη ξεραίνεται στὸν ἀέρα καὶ στὴ συνέχεια ἐκχυλίζεται μὲ πετρελαϊκὸ αἰθέρα. Τὸ προϊὸν τῆς ἐκχυλίσεως ὑποβάλλεται σὲ TLC ἀνάλυση, ἀποτέλεσμα τῆς ὁποίας εἶναι ἡ ἐμφάνιση τεσσάρων κηλίδων μὲ R_f 0,95, 0,64, 0,12 καὶ 0,06.

Ἐπακολουθεῖ χρωματογραφικὴ ἀνάλυση στήλης τοῦ προϊόντος τῆς ἐκχυλίσεως, τὰ ἀποτελέσματα τῆς ὁποίας δίνονται στὸν πίνακα I.

Ἡ ὑδρογονανθρακικῆς συστάσεως ὁμάδα κλασμάτων (κλάσματα 1 καὶ 2 τοῦ πίνακα I) ὑποβάλλεται σὲ GLC ἀνάλυση[3] καὶ διαχωρίζεται σὲ ἕνδεκα συστατικὰ (διάγραμμα 1).

Ἡ ταυτοποίηση τῶν κορυφῶν τοῦ χρωματογραφήματος ἔγινε μὲ τὴ βοήθεια φασμάτων μάζης. Ἔτσι, ἡ ἐξέταση τῶν φασμάτων μάζης τῶν κορυφῶν τοῦ χρωματογραφήματος (διάγραμμα 1) ἔδωσε τὸ ἀκόλουθο ἀποτέλεσμα.

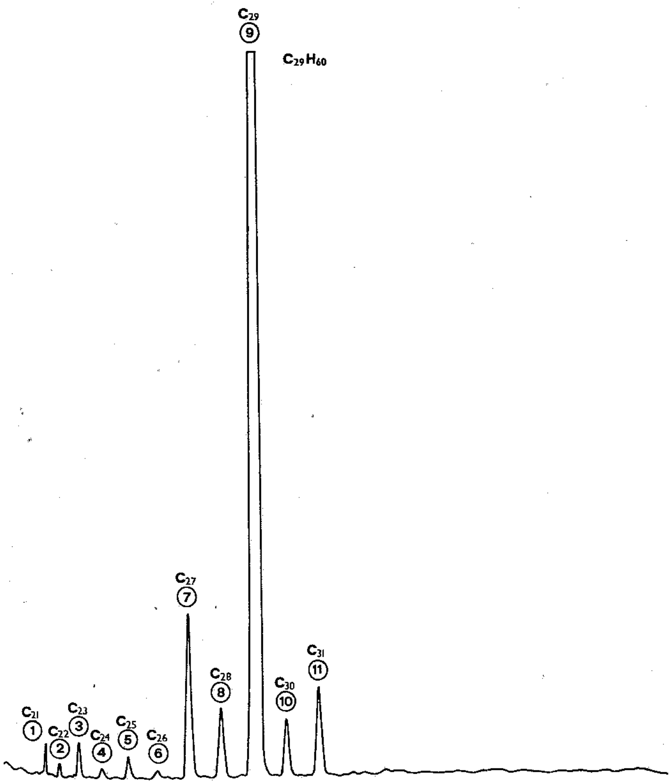
Ἀπὸ τὸν πίνακα II προκύπτει ὅτι τὸ βασικὸ συστατικὸ τοῦ ὑδρογονανθρακικοῦ μέρους τοῦ μίγματος τῶν κηρῶν εἶναι ὁ ὑδρογονάνθρακας $C_{29}H_{60}$. Γενικὰ ἡ ἀναλογία τῶν ὑπόλοιπων ὑδρογονανθράκων αὐξάνεται ὅσο πλησιάζουν πρὸς τὸ C_{29}.

Πειραματικὸ μέρος

Ἀπομόνωση τῶν κηρῶν: 200 gr ξηρῆς κονιοποιημένης δρόγης ἐκχυλίζεται σὲ συσκευὴ Soxhlet ἐπὶ 48 ὧρες μὲ πετρελαϊκὸ αἰθέρα (σ.ζ. 40-60°C). Μετὰ τὴν ἀπομάκρυνση τοῦ πετρελαϊκοῦ αἰθέρα παραμένει στερεὸ βάρους 3,132 gr.

Πίνακας Ι: *Χρωματογραφικὴ ἀνάλυση στήλης τῶν κηρωδῶν συστατικῶν τοῦ Hypericum perforatum*

α/α κλάσματος	Ἐκλουστικὸ μέσο	Βάρος κλάσματος (gr)	R_f
1-2	πετρελαϊκὸς αἰθέρας	0,520	0,95
3-5	πετρελαϊκὸς αἰθέρας	0,780	0,64
6-11	πετρελαϊκὸς αἰθέρας	0,330	0,06 καὶ 0,64
12-13	πετρ. αἰθέρας-βενζόλιο (90+10)	0,090	0,06, 0,12, 0,35 καὶ 0,64
14-15	πετρ. αἰθέρας-βενζόλιο (75+25)	0,100	0,06, 0,12 καὶ 0,64
16-17	πετρ. αἰθέρας-βενζόλιο (50+50)	0,150	0,06 καὶ 0,12
18-24	πετρ. αἰθέρας-βενζόλιο (50+50)	0,800	0,06
25-28	βενζόλιο	0,085	0,06
29-31	βενζόλιο-χλωροφόρμιο (90+10)	0,035	0,06
32-34	βενζόλιο-χλωροφόρμιο (75+25)	0,035	0,06
35-38	βενζόλιο-χλωροφόρμιο (50+50)	0,160	0,06
39-42	χλωροφόρμιο	0,040	0,06



Διάγραμμα 1: *GLC ἀνάλυση τοῦ ὑδρογονανθρακικοῦ μέρους τοῦ μίγματος τῶν κηρωδῶν συστατικῶν τοῦ Hypericum perforatum.*

Πίνακας II: *Ὑδρογονάνθρακες τῶν κηρωδῶν συστατικῶν τοῦ Hypericum perforatum*

Κορυφὲς χρωματογραφήματος διαγράμματος 1	MS	Τύπος	%
1	M^+296	$C_{21}H_{44}$	0,701
2	M^+310	$C_{22}H_{46}$	0,172
3	M^+324	$C_{23}H_{48}$	0,803
4	M^+338	$C_{24}H_{50}$	0,303
5	M^+352	$C_{25}H_{52}$	0,620
6	M^+366	$C_{26}H_{54}$	0,170
7	M^+380	$C_{27}H_{56}$	5,708
8	M^+394	$C_{28}H_{58}$	2,675
9	M^+408	$C_{29}H_{60}$	82,895
10	M^+422	$C_{30}H_{62}$	2,283
11	M^+436	$C_{31}H_{64}$	3,783

Χρωματογραφικὸς διαχωρισμός: Τὸ προϊὸν τῆς ἐκχυλίσεως ὑποβάλλεται σὲ TLC ἀνάλυση πάνω σὲ ἕτοιμη πλάκα (Merck), μὲ προσροφητικὸ ὑλικὸ Kieselgel 60 F_{254}. Ὡς ὑγρὸ ἀναπτύξεως χρησιμοποιεῖται μίγμα πετρελαϊκοῦ αἰθέρος βενζολίου (65+35). Μετὰ τὴν ἀνάπτυξη ἡ πλάκα ψεκάζεται μὲ διάλυμα θειικοῦ ὀξέος (70%) ποὺ περιέχει 0,5% θειικὸ χαλκὸ καὶ στὴ συνέχεια θερμαίνεται στοὺς 150°C ἐπὶ 15 min. Μὲ τὸν τρόπο αὐτὸν ἐμφανίζονται τέσσερεις κηλίδες μὲ R_f 0,95, 0,64, 0,12 καὶ 0,06.

Τὸ στερεὸ ὑπόλειμμα τῆς ἐκχυλίσεως διαλύεται σὲ χλωροφόρμιο, ὑποβάλλεται σὲ ξήρανση καὶ μεταφέρεται στὴν κορυφὴ στήλης ὕψους 45cm καὶ διαμέτρου 3cm, γεμισμένης μὲ 200gr Kieselgel 60 (70-230 mesh). Ἡ στήλη ὑποβάλλεται σὲ ἔκλουση μὲ διάφορα ἐκλουστικὰ μέσα (πίνακας I) τῶν 25ml. Ἡ σύσταση κάθε κλάσματος ἐξετάζεται μὲ TLC ἀνάλυση καὶ τὰ κλάσματα τῆς ἴδιας συστάσεως συνενώνονται σὲ ὁμάδες.

Ὑδρογονάνθρακες: Ἡ ὑδρογονανθρακικῆς συστάσεως ὁμάδα κλασμάτων κρυσταλλώνεται ἀπὸ ἀκετόνη μὲ τὴ μορφὴ λαμπερῶν καὶ ἄχροων φυλλιδίων σ.τ. 69-71°C.

Ἡ ἐξέταση τοῦ φάσματος IR ἔδειξε ἀπορροφήσεις μόνον ὑδρογονανθρακικῶν δεσμῶν, μὲ τὴν χαρακτηριστικὴ διπλῆ κορυφὴ τῶν στερεῶν ἀλκανίων (725 καὶ 715cm^{-1}) γιὰ τὴν ὁμάδα $—(CH_2)_n—$ ($n \geq 4$).

Ἡ παραπάνω ὁμάδα κλασμάτων ὑποβλήθηκε σὲ GLC ἀνάλυση μὲ ἀεριοχρωματογράφο τύπου Varian-Aerograph 1520 μὲ ἀνιχνευτὴ ἰονισμοῦ φλογὸς (FID). Χρησιμοποιήθηκε στήλη μήκους 0,37m καὶ διαμέτρου 2mm, γεμισμένη μὲ Chromosorb G (MS7, 3% SE 30). Προγραμματισμένη θερμοκρασία 100-300°C μὲ ταχύτητα 10°/min. Φέρον ἀέριον He παροχῆς 25ml/min. Ταχύτητα χαρτιοῦ 0,2inch/min.

Εὐχαριστῶ τὸν Dr. R. Moser γιὰ τὴ λήψη τῶν φασμάτων μάζης

Abstract

The Hydrocarbon Composition of Waxes of Hypericum perforatum

The isolation and identification of the hydrocarbon substances of the waxes of the plant Hypericum perforatum is described.

From the investigation it arises that the mixture of the wax substances of this plant consisted of hydrocarbons and some other susbstances probably esters and highmolecule alcohols the structure of which haven't been identified yet.

The mixture of the hydrocarbons consisted mainly of eleven saturated unbranched hydrocarbons C_{21}-C_{31}. Among them the C_{29} member represents the major constituent (83%).

Βιβλιογραφία

1 Thomson, R.H.: *"Naturally Occuring Quinones"*, 2nd Ed., p. 586, 587, 591, Academic Press, London, (1971)

2 Brockmann, H.: *Proc. Chem. Soc.*, 304, (1957); *Prog. Chem. Org. Nat. Prods.* **14**, 142 (1957)

3 Eckert, M.: *Sonderdruck aus fette' seifen' anstrichmittel*, **75**, 150 (1973); Industrieverlag von Hernhaussen KG, Hamburg 11.

Notes

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THE RELATION BETWEEN THE VOLUME VIRIAL COEFFICIENTS AND THE PRESSURE VIRIAL COEFFICIENTS

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A simple method is presented for obtaining the relations between the volume virial coefficients and the pressure virial coefficients. The first six volume (pressure) coefficients as a function of pressure (volume) coefficients are given.

The virial equation of state in powers of the density is written in the form:

$$Z=\frac{Pv}{RT}=1+\sum_{j=1} A_j v^{-j} \qquad (1)$$

where $v=\frac{V}{n}$

is the molecular volume. An entirely anologous to (1) expression in which the pressure is substituted for the density is as follows:

$$Z=\frac{Pv}{RT}=1+\sum_{k=1} B_k P^k \qquad (2)$$

The coefficients A_1, A_2,... and B_1, B_2,... are functions of the temperature only, and the forms of these functions depend on the types of intermolecular forces in the gas. The series (2) is mathematically equivalent to the series (1) and the coefficients of the two series are uniquely related to each other.

Several procedures[1-6] have been proposed to derive the relations between the coefficients of (2) and those of (1). Despite the simplicity of a recently proposed method,[6] it is still quite tedious for one to obtain relations between the higher terms of (1) and (2). It is the purpose of this note to present a very simple and straightforward method for obtaining these relations.

Eq. (1) can be solved with respect to P:

$$P=\frac{RT}{v}\left(1+\sum_{j=1} A_j v^{-j}\right) \qquad (3)$$

By equating the right-hand sides of Equations (1) and (2) we obtain:

$$\sum_{j=1} A_j v^{-j} = \sum_{k=1} B_k P^k \tag{4}$$

Substituting equation (3) into (4), the last is transformed as follows:

$$\sum_{j} A_j v^{-j} = \sum_{k} B_k \, (RTv^{-1})^k (1 + \sum_{j} A_j v^{-j})^k \tag{5}$$

By grouping the terms of the same power in v on the right hand side of equation (5) and equating them with the corresponding terms on the left hand side of equation (5) we can obtain the relation we are looking for. The term

$$(1 + \sum_{J} A_j v^{-j})^k$$

of equation (5) can be expanded using the well known formula of polynomial expansion:

$$(\beta_1 + \beta_2 + \ldots + \beta_m)^\lambda = \sum \frac{\lambda!}{\lambda_1!\ \lambda_2!\ \ldots\ \lambda_m!} \beta^\lambda{}_1 \beta^\lambda{}_2 \ldots \beta^\lambda{}_m \tag{6}$$

where the summation includes all different combinations of λ_1, λ_2, ... λ_m with

$$\sum_{i=1} \lambda_i = \lambda$$

and λ_i and λ are all integrals.

As an example we apply equation (5) in combination with formula (6) for $j = k = 6$:

$$\begin{aligned} \frac{A_1}{v} + \frac{A_2}{v^2} + \ldots + \frac{A_6}{v^6} + \ldots = {} & B_1 \frac{RT}{v} \left(1 + \frac{A_1}{v} + \frac{A_2}{v^2} + \ldots + \frac{A_6}{v^6} + \ldots\right) + \\ & + B_2 \left(\frac{RT}{v}\right)^2 \left(1 + \frac{A_1}{v} + \frac{A_2}{v^2} + \ldots + \frac{A_6}{v^6} + \ldots\right)^2 + \ldots \\ & + B^6 \left(\frac{RT}{v}\right)^6 \left(1 + \frac{A_1}{v} + \frac{A_2}{v^2} + \ldots + \frac{A_6}{v^6} + \ldots\right)^6 + \ldots \end{aligned} \tag{7}$$

From equation (7) we obtain:

$$\begin{aligned} B_1 &= \frac{A_1}{RT} \\ B_2 &= \frac{A_2 - A^2{}_1}{(RT)^2} \\ B_3 &= \frac{A_3 - 3A_1A_2 + 2A^3{}_1}{(RT)^3} \\ B_4 &= \frac{A_4 - 4A_1A_3 + 10A^2{}_1A_2 - 5A^4{}_1 - 2A^2{}_2}{(RT)^4} \end{aligned} \tag{8}$$

$$B_5 = \frac{A_5 - 5A_1A_4 - 5A_2A_3 + 15A_1A_2^2 + 15A_1^2A_3 - 35A_1^3A_2 + 14A_1^5}{(RT)^5}$$

$$B_6 = \frac{\dfrac{A_6 - 6A_1A_5 - 6A_2A_4 + 42A_1A_2A_3 + 21A_1^2A_4 - 84A_1^2A_2^2 - 56A_1^3A_3 +}{126A_1^4A_2 - 42A_1^6 + 7A_2^3 - 3A_3^2}}{(RT)^6} \qquad (8)$$

An interesting observation concerning the numerical coefficients of the numerators in the expressions (8), is that their algebraic sum in each term (with the obvious exception of the first term, B_1) is zero.

The relations (8) can be inverted to give:

$A_1 = RTB_1$
$A_2 = (RT)^2 (B_2 + B_1^2)$
$A_3 = (RT)^3 (B_3 + 3B_1B_2 + B_1^3)$
$A_4 = (RT)^4 (B_4 + 4B_1B_3 + 6B_1^2B_2 + B_1^4 + 2B_2^2)$
$A_5 = (RT)^5 (B_5 + 5B_1B_4 + 5B_2B_3 + 10B_1B_2^2 + 10B_1^2B_3 + 10B_1^3B_2 + B_1^5)$
$A_6 = (RT)^6 (B_6 + 6B_1B_5 + 6B_2B_4 + 30B_1B_2B_3 + 20B_1^3B_3 + 15B_1^2B_4 + 30B_1^2B_2^2 + 15B_1^4B_2 + B_1^6 + 5B_2^3 + 3B_3^2)$

The first four terms given in Eqs. (8) are in exact agreement with the results given by L. Epstein,[2,3] W. Putman — E. Kilpatrick[4] and S. Vassiliadou-Athanassiou — Th. Yannakopoulos.[6]

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Περίληψις

Ἡ σχέσις μεταξὺ τῶν συντελεστῶν virial ὄγκου καὶ συντελεστῶν virial πιέσεως.

Παρουσιάζεται μέθοδος συσχετίσεως τῶν συντελεστῶν virial ὄγκου καὶ τῶν συντελεστῶν virial πιέσεως. Ἂν καὶ ἡ μέθοδος στερεῖται μαθηματικῆς κομψότητος καὶ δὲν δίδονται γενικοὶ ὅροι, ἐν τούτοις εἶναι ἁπλουστέρα τῶν ἤδη ὑπαρχουσῶν μεθόδων καὶ ἔχει πρακτικὴν σημασίαν. Ὡς παράδειγμα ἐφαρμογῆς παράγονται οἱ πρῶτοι ἓξ (συμβατικῶς ἑπτὰ) συντελεσταὶ virial ὄγκου ὡς συνάρτησις τῶν συντελεστῶν virial πιέσεως.

References and Notes

1 Reid, R. and Sherwood, T.: *"The Properties of Gases and Liquids"*, Editor McGraw Hill Book Co. (1966).
2 Epstein, L. F.; *J. Chem. Phys.*, **20**, 1981 (1952).
3 Epstein, L.F.: *J. Chem. Phys.*, **21**, 762 (1953).
4 Putnam, W.E. and Kilpatrick, J.E.: *J. Chem. Phys.*, **21**, 951 (1953).
5 Kilpatrick, J.E. and Ford, D.I.: *Am. J. Phys.* **37**, 881 (1969).
6 Vassiliadou-Athanassiou, S. and Yannakopoulos, Th.: *J. Phys. Chem.*, **99**, 154 (1976).